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Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options Volume XVI. Sulfur Oxides Summary Report

Arthur D. Little, Inc., Cambridge, MA

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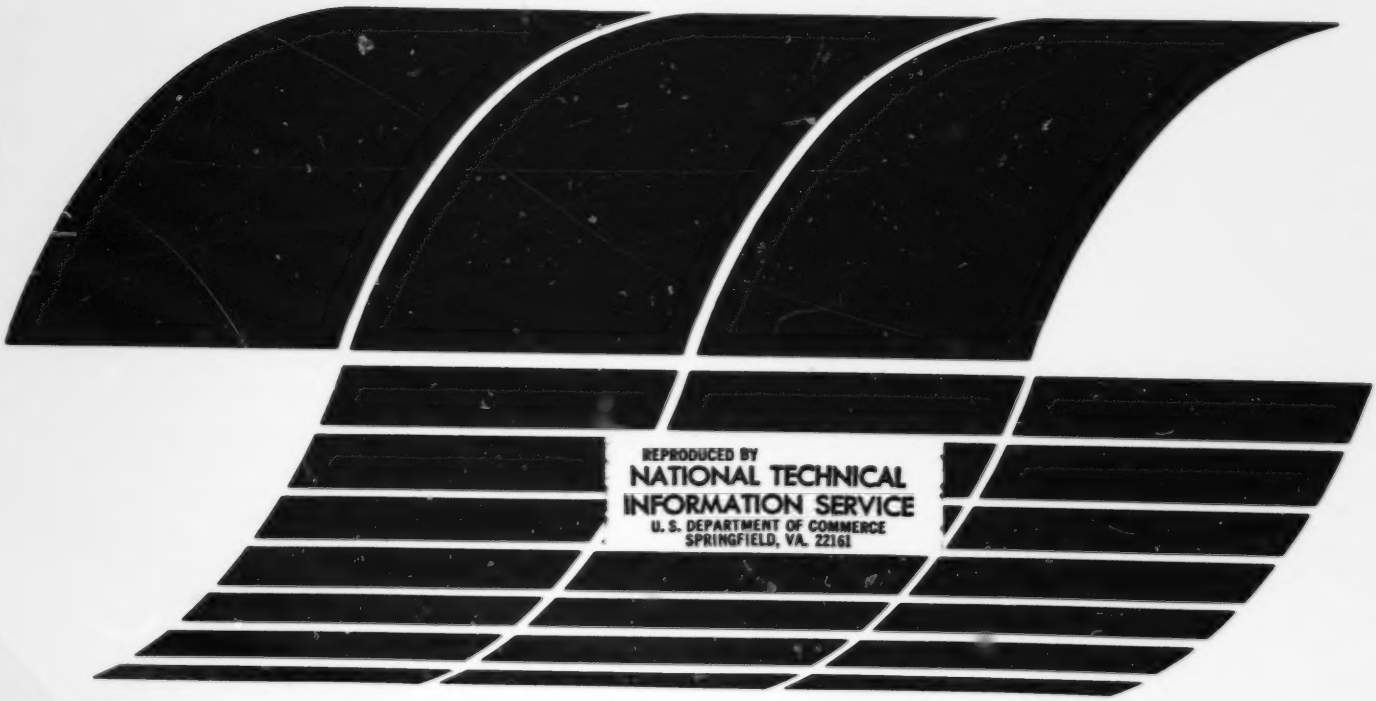
Volume XVI. Sulfur Oxides Summary Report

Interagency Energy/Environment R&D Program Report



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This present report summarizes the information regarding sulfur oxide pollutants in the 13 industry reports. Four parallel reports treat nitrogen oxides, particulates, solid residues, and toxics/organics. All of these pollutant-oriented reports are intended to be closely used with the original 15 reports.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY-CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XVI. Sulfur Oxides Summary Report

by

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Contract No. 68-03-2198

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment, and even on our health, often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report summarizes information on sulfur oxides from a study of 13 energy-intensive industries. If implemented over the coming 10 to 15 years, these processes and practices could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives.

The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary.

Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction.

The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Under EPA Contract No. 68-03-2198, Arthur D. Little, Inc. undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options." Some 80 industrial process options were examined in 13 industrial sectors. Results were published in 15 volumes, including a summary, industry prioritization report, and 13 industry oriented reports (EPA-600/7-76-034 a through o).

This present report summarizes the information regarding particulates in the 13 industry reports. Four parallel reports treat sulfur oxides, nitrogen oxides, solid residues, and toxics/organics. All of these pollutant-oriented reports are intended to be closely used with the original 15 reports.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	$Metre^2$	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	$Metre^3$	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t_C^o = (t_F^o - 32)/1.8$
Degree Rankine	Degree Kelvin	$t_K^o = t_R^o/1.8$
Foot	Metre	0.3048
$Foot^3$/minute	$Metre^3$/sec	0.0004719
$Foot^3$	$Metre^3$	0.02831
$Foot^2$	$Metre^2$	0.09290
Foot/sec	Metre/sec	0.3048
$Foot^2$/hr	$Metre^2$/sec	0.00002580
Gallon (U.S. liquid)	$Metre^3$	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	$Metre^3$	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (Assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

SECTION 1

INTRODUCTION

BACKGROUND AND PURPOSE

During 1975 and the first half of 1976, under EPA Contract No. 68-03-2198, Arthur D. Little, Inc., undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options" in 13 energy-intensive industry sectors for the U.S. Environmental Protection Agency (EPA). The results of these studies were published in the following reports:

- Volume I -- Industry Summary Report (EPA-600/7-76-034a)
- Volume II -- Industry Priority Report (EPA-600/7-76-034b)
- Volume III -- Iron and Steel Industry (EPA-600/7-76-034c)
- Volume IV -- Petroleum Refining Industry (EPA-600/7-76-034d)
- Volume V -- Pulp and Paper Industry (EPA-600/7-76-034e)
- Volume VI -- Olefins Industry (EPA-600/7-76-034f)
- Volume VII -- Ammonia Industry (EPA-600/7-76-034g)
- Volume VIII -- Alumina/Aluminum Industry (EPA-600/7-76-043h)
- Volume IX -- Textiles Industry (EPA-600/7-76-034i)
- Volume X -- Cement Industry (EPA-600/7-76-034j)
- Volume XI -- Glass Industry (EPA-600/7-76-034k)
- Volume XII -- Chlor-Alkali Industry (EPA-600/7-76-0341)
- Volume XIII -- Phosphorus/Phosphoric Acid Industry (EPA-600/7-76-034m)
- Volume XIV -- Copper Industry (EPA-600/7-76-034n)
- Volume XV -- Fertilizer Industry (EPA-600/7-76-034o)

In the course of this study, some 80 industrial process options were examined, focusing on:

- Identification of any major sources and amounts of pollutants (air, water and solid) expected from the processes,
- Development of estimated capital and operating costs for both production and pollution control aspects of the processes,
- Estimation of the types and amounts of energy used in both production and pollution control for the processes,
- Assessment of the economic viability and likelihood of implementation of those alternative process options being studied,
- Identification of areas where EPA's activities and policies could influence the future choice of alternatives, and
- Identification of research and development areas in both process and pollution control technology.

Because of the industry orientation of the study (encompassing 15 volumes and some 1,700 pages), it was felt that pollutant-specific information across all the 13 sectors studied should be summarized. Five such pollutants were identified to be of particular interest:

- Nitrogen oxide (NO_x) emissions,
- Sulfur oxide (SO_x) emissions,
- Fine particulate emissions,
- Solid residues, and
- Organic and/or toxic pollutants.

A summary pollutant report in each of these areas has been prepared. Although we did attempt some estimates and extrapolations on pollutants where information was readily available, in general, we did not attempt to go beyond the contents of the 15 original reports.

APPROACH

These summary pollutant reports are intended to be used closely with the original 15 reports. Generally, information, such as detailed descriptions of the processes, has not been duplicated in these pollutant reports. Sections of the previous 15 reports in which this information can be found have been extensively referenced by volume number and page number (e.g., Volume VII, page 20, refers to page 20 of the Ammonia Industry report).

TABLE 1. PROJECTED U.S. PRODUCTION IN INDUSTRIES STUDIED

Commodity	Total U.S. production in 1974 (10^6 tons*)	Projected rate of growth (%/yr)	Total projected production in 1989 (10^6 tons)	Increase in annual production in 1989 over that of 1974 (10^6 tons)
Alumina	7.7	6.0	18.5	10.75
Aluminum	5.0	6.0	12.0	7.0
Ammonia	9.2	6.0	22.0	12.8
Cement	79.0	2.0	106.3	27.3
Chlorine	11.0	5.0	22.9	11.9
Coke	62.0	2.5	89.8	27.8
Copper	1.6	3.5	2.7	1.1
Fertilizers (HNO_3)	8.2	4.0	14.8	6.6
Glass (flat)	29.0	2.5	42.0	13.0
Iron	100.0	2.5	144.8	44.8
Olefins (ethylene)	13.0	8.0	41.2	28.2
Petroleum	740.0**	1.5	925.0***	185.0****
Pulp (kraft)	16.0	5.0	33.3	17.3
Pulp (newsprint)	3.9	2.5	5.6	1.7
Phosphoric Acid (detergent grade)	1.4	2.5	2.03	0.63
Phosphoric Acid (wet acid grade)	9.0	2.5	13.0	4.0
Steel	133.0	2.5	193.0	60.0
Textiles (knit)	0.32	2.2	0.44	0.12
Textiles (woven)	2.1	2.2	2.91	0.81

*All tons referred to in these reports are net tons, unless otherwise indicated.

**Approximate equivalent of 30 quads (1 quad is equal to 10^{15} Btu).

***Approximate equivalent of 37.5 quads.

****Approximate equivalent of 7.5 quads.

In Section 2 of this report (Findings and R&D Overview), summary information on generic, cross-industry problems that emerge and suggestions for research and development work in the areas of both pollution control technology and process technology are presented. In Section 3 of this report, availability and applicability of SO_x pollution control technology is presented, and SO_x emissions and controls reported in our previous study are summarized. Unless otherwise noted, the SO_x in gas streams is largely SO_2 with only 1 to 3 percent of the sulfur values reported as SO_3. All emissions are estimated unless specifically referenced, since we believe that actual data do not exist for many of the processes described, which are frequently still under development.

To give the reader a sense of the size of the industries for which the pollution problems covered in these summary pollutant reports are considered, Table 1 lists these industries, their total production in 1974 (the baseline year for the study), and their projected incremental production in 1989 -- 15 years hence.

SECTION 2

FINDINGS AND R&D OVERVIEW

FINDINGS

Eight of the 13 industries addressed in the original study have process-related SO_x emissions that are affected by potential process changes and are reviewed in this report. These industries are petroleum refining, cement, olefins, ammonia, alumina/aluminum, pulp and paper, glass, and copper. In addition, process changes in the remaining five industries show changes for steam and/or electric energy requirements and thus SO_x emissions are affected at the generating source. Table 2-1 lists the estimated SO_x emissions from processes, steam, and power boilers for both the base case and alternative processes and process alternatives for these industries.

The SO_x emission shown in the table include both process and power boiler emissions. Emissions from the power boiler were generally not considered in the original study, but are included here because emissions from the base case and alternative processes are compared in this report. The power boilers include on-site power boilers for steam and electricity generation. The emissions represent controlled emissions from the process as further described in Section 3 where it is seen that the emission factors vary from less than 1 lb of SO_x/ton of product to more than 1400 lb of SO_x/ton of product as found in the copper industry. The emission factors from the conventional smelter in the copper industry are high because of both high sulfur content in the ore and an absence of economical control technology for reverberatory furnace off-gas. The emissions for the aluminum industry range from an estimated 138 lb of SO_x/ton to 200 lb of SO_x/ton. These high emissions result mostly from power boilers, because the production of aluminum requires large quantities of electricity which we assume will be generated largely from coal to meet incremental aluminum production requirements.

As shown in Table 2, the petroleum industry was responsible for the greatest volume of emissions of sulfur compounds from the base case process in the year 1974, followed by copper, aluminum, kraft, pulp, cement, and so forth. Table 2 also shows estimated incremental SO_x emissions (1989 - 1974) based on the increase in annual production from 1974 to 1989. Incremental emissions are shown from both the base case and alternative processes, assuming dedication of 100% of the incremental production rather than a fraction to each process (base case and alternative). Thus incremental SO_x emissions (1989 - 1974) are calculated by multiplying the emission factors (lb SO_x per ton of product (e.g., copper) by the increase in production of product between 1974 to

TABLE 2. SUMMARY OF ESTIMATED ANNUAL SO_x EMISSIONS

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Petroleum	Base case:			
	East Coast refinery	3,030****	758****	--
	• Direct combustion of asphalt in process heaters and boilers	--	840****	+82****
	• Flexicoking	--	803****	+45****
	Base case:			
	Gulf Coast refinery	1,230****	308****	--
	• On-site electric power by combustion of vacuum bottoms	--	308****	0
	Base case:			
	West Coast refinery	2,580****	645****	--
	• Hydrocracking of heavy bottoms	--	728****	+83****
	• High-purity hydrogen via partial oxidation of asphalt	--	653****	+8****

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Cement	Base case : Long dry kiln	553	191	--
	• Suspension preheater	--	183	-8
	• Flash calciner	--	183	-8
	• Fluidized bed	--	134	-57
	• Coal as fuel instead of gas in long dry kiln	--	516	+325
Olefins	Base case : Ethane-Propane Process	28.6	62	--
	• Naphtha process	--	102	+40
	• Gas-oil process	--	361	+299
Ammonia	Base case : Ammonia via natural gas	5.5	7.7	--
	• Ammonia via coal gasification	--	30.7	+23
	• Ammonia via heavy fuel oil	--	20.5	+12.8

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from Base Case Process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Alumina	Base case: Bayer process	25.4	36	--
	• Hydrochloric acid ion exchange	--	18	-18
	• Nitric acid ion exchange	--	663	+627
	• Toth alumina	--	153	+117
Aluminum	Base case: Hall-Heroult (current practice, C.P.)	1,045	1,463	--
	• Hall-Heroult (new)	--	1,113	-350
	• Alcoa chloride	--	966	-497
	• Refractory hard metal cathode	--	1,183	-280
	Base case: Bayer with Hall-Heroult (C.P.)	1,070	1,505	--
	• Clay Chlorination (Toth alumina) and Alcoa chloride	--	1,043*****	-462*****

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
	Base case:			
	Kraft pulping	766	829	0
	• Alkaline oxygen pulping	--	59	-770
	• Rapson effluent-free Kraft pulping	--	844	+15
Newsprint pulp	Base case:			
	Refiner mechanical pulp (RMP)	96	42	0
	• Thermo-mechanical pulp (TMP)	--	34	-8
	• De-inking of old news for newsprint manufacture	--	12	-30
Flat glass	Base case:			
	Regenerative furnace	27.3	12.2	0
	• Coal Gasification	--	13.1	+0.9
	• Direct coal firing	--	43.4	+31.2
	• Coal-fired hot gas generation	--	16.1	+3.9

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Flat glass (cont.)	• Electric melting	--	129	+117
	• Batch preheat with natural gas firing	--	10.4	-1.8
Copper	Base case: Conventional smelting	2,250	1,550	0
	• Outokumpu flash smelting	--	152	-1,398
	• Noranda	--	152	-1,398
	• Mitsubishi	--	152	-1,398
	• Arbiter	--	68	-1,482
Chlorine, NaOH	Base case: Graphite-anode diaphragm cell	454	491	--
	• Dimensionally stable anodes	--	472	-19.0
	• Expandable DSA	--	424	-67.0
	• Polymer modified asbestor	--	455	-36.0

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Chlorine, NaOH (cont.)	• Polymer membrane	--	455	-36.0
	• Ion exchange membrane	--	447	-44.0
	• Mercury cell	--	557	+66
Steel	Base case: No off-gas recovery	16.4	12.0	--
	• Off-gas recovery	--	6.0	-6.0
Blast furnace hot metal	Base case: Blast furnace	30	13.4	--
	• Blast furnace with external desulfurization	--	13.4	0.0
Coke	Base case: Wet quenching of coke	N.A.	N.A.	--
	• Dry quenching of coke	--	-30.6******	-30.6******

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Steel (integrated)	Base case: Steelmaking coke oven, blast furnace BOP route	189	138	--
	• Direct reduction, EAF route	--	540	+402.0
Phosphoric acid (detergent grade)	Base case: Electric furnace	100	45	--
	• Chemical cleanup of wet-process acid	--	8.4	-36.6
	• Solvent extraction of wet-process acid	--	5.9	-39.1
Fertilizers (nitric acid)	Base case: No NO_x control	-3.3	-2.6	--
	• Catalytic reduction	--	-4.0	-1.4
	• Molecular sieve	--	75.2	+77.8
	• Grand paroisse	--	0.66	+3.26
	• CDL/Vitak	--	209.0	+212.0

TABLE 2. (continued)

Commodity	Process	Controlled SO_x emissions in 1974 from base case process (10^6 lb/yr)	Controlled SO_x emissions (1989-1974)** (10^6 lb/yr)	Change in SO_x emissions from base case (in 1989)*** (10^6 lb/yr)
Fertilizers (cont.)	• Masar	--	383.0	+386.0
Fertilizers (mixed):	Converting fertilizer dryers (with baghouses) from natural gas to oil.			
	Base case: Natural gas	Nil	Nil	Nil
	• Better equipment technique with fuel oil	--	0.29	0.29
	• Installing scrubbers	--	0.22	0.22
Textiles	Knit fabric:			
	• Base case-- conventional aqueous	2.9	1.1	--
	• Advanced aqueous	--	1.0	-0.1
	• Solvent processing	--	0.5	-0.6
	Woven fabric:			
	• Base case	50.0	19.3	--
	• Advanced aqueous	--	8.8	-10.5

TABLE 2. (continued)

*Except where denoted by superscript ****.

**Based on incremental production from the year 1974 to 1989 derived from anticipated growth rates (Table 1).

***Assumes no retirement of existing facilities by 1989.

****National emission rates calculated as though the alternative process applies to all national oil refinery production.

*****Bayer process, plus Hall-Heroult (new plant) process, is used for comparative analysis.

******Change estimated from base case.

N.A. not available.

1989. Total actual emissions from each process for the year 1989 would be the sum of 1974 emissions from the base case process assuming no retirement of existing facilities and the actual incremental emissions per year from the base case and new processes installed between 1974 and 1989.

The estimated increase or decrease in emissions from the alternative processes in relation to the base case process is also shown in Table 2 for the year 1989. This number shows the potential for emission reduction in 1989 using new process technology. It is seen that the greatest potential for emission reduction by new processes exists in the copper industry, followed by the kraft pulp and aluminum industries.

In the copper industry, alternative processes using smelters are aimed at generating gas that has a sufficiently high concentration of SO_x, so that the SO_x can be controlled by installing sulfuric acid plants. Thus, these processes would have lower SO_x emissions.

In the kraft pulp industry, compounds containing sulfur are not used in alkaline oxygen pulping, which eliminates emissions that contain sulfur compounds.

The alternative processes in the aluminum industry are aimed at reducing power consumption, which results in lower SO_x emissions at the power boilers.

Some of the processes studied are aimed at changing the form value of fuel from natural gas or oil to coal or asphalt. These process changes would generally result in increased SO_x emissions because of higher sulfur content in the fuel. This is seen in the petroleum, cement, alumina, and glass industries. The effect of changing from low-sulfur feedstock to high-sulfur feedstock is seen in the olefin industry and results in increased SO_x emissions.

To give some perspective to the magnitude of SO_x emissions, Table 3 shows the industrial processes category to be the second largest emitter of SO_x after electric utilities.

TABLE 3 SO_x NATIONWIDE EMISSION ESTIMATES (1974)

Emission source	10^6 lb/yr	% of total
Stationary fuel combustion		
- Electric utilities	42,200	61.9
- Other	11,400	16.7
Industrial processes	12,600	18.5
Transportation	1,600	2.3
Solid waste	200	0.3
Miscellaneous	200	0.3
TOTAL	68,200	100.0

Source: National Air Quality and Emissions Trend Report, 1975, EPA, Research Triangle Park, N.C.; NTIS PB-263 922

Should U.S. industry expand using current (base case) technology, Table 4 shows that estimated controlled SO_x emissions in 1989 would increase by 5.6×10^9 lb compared to SO_x emissions of 12.6×10^9 lb from industrial processes and 42.2×10^9 lb from utilities in 1974 (Table 3). However, if all U.S. industry expanded by implementing the technologies considered here that emitted the largest amounts of SO_x, Table 4 shows that the increase in SO_x emissions in 1989 would be 8.0×10^9 lb, or some 43% higher than using conventional technology. On the other hand, if industry expanded by implementing the least SO_x-emitting technology, SO_x emissions in 1989 are calculated to increase by 2.6×10^9 lb or some 54% less than by conventional technology. If the national production growth rate projections shown in Table 1 are accurate, then calculated emissions will probably lie somewhere between these extremes, with energy (Btu) saving processes with lower SO_x emissions somewhat balancing the switch from natural and fuel oil to coal. Thus, incentives for the implementation of energy conserving technology can have a significant effect on future SO_x emissions in the industrial sector.

Table 5 shows our estimate of the types of processes likely to be installed in the time period up to 1989 with related SO_x emissions from new plants calculated for the year 1989 assuming no retirement of existing facilities. For example, a reading of the industry reports shows that in the copper sector incremental copper smelting capacity will be effected by one of the newer oxygen or flash smelting processes (e.g., Outokumpu 4, Noranda, Mitsubishi). If such capacity is installed, anticipated annual SO_x emissions in 1989 would be 152×10^9 lb SO_2/yr (Table 5) compared to the $1,550 \times 10^9$ lb SO_2/yr, if conventional reverberatory furnace technology were employed. Similar judgments were made in other sectors to arrive at total calculated annual emissions of 2.4 to 5.6×10^9 lb SO_2 emitted in 1989 from new plant capacity installed in the period 1974 - 1989.

Examination of the last column in Table 2 shows that greatest reduction compared to the base case process in lb of SO_x emissions per year can be achieved by selective implementation of new processes in -

- copper (oxygen or flash processes)
- aluminum (Alcoa chloride, refractory hard metal cathodes)
- pulp (alkaline-oxygen)

Process changes in some of the industries shown in Table 2 may be implemented because of feed stock shortages (e.g., the manufacture of olefins from low-sulfur naphtha rather than higher sulfur gas oil), and fuel switching (e.g., use of coal in cement making). In other cases, processes may be developed for other reasons, such as development of a domestic alumina industry based on indigenous kaolin clays. Such a process, based on using coal to the extent possible, would

TABLE 4. ESTIMATED INCREASE IN CONTROLLED SO_x EMISSIONS 1989-1974 ASSUMING INDUSTRY EXPANDS USING PROCESS TYPES INDICATED (10^6 lbSO_2/yr)

Commodity(vol no)*	Base case process	Using process with largest potential SO_x emissions	Using process with smallest potential SO_x emissions
Steel (III)	138	540	101***
Petroleum (IV)	758**	840	758
Kraft pulp (V)	829	844	59
Newsprint pulp (V)	42	42	12
Olefins (VI)	62	361	62
Ammonia (VII)	8	31	8
Alumina (VIII)	36	663	18
Aluminum (VIII)	1,463	1,463	966
Textiles-knit (IX)	1	1	< 1
Textiles-woven (IX)	19	19	9
Cement (X)	191	516	134
Flat glass (XI)	12	129	12
Chlorine, NaOH (XII)	491	557	424
Phosphoric acid (XIII)	45	45	6
Copper (XIV)	1,550	1,550	68
Fertilizers(HNO_3) (XV)	-3****	383	-4
TOTAL	5,642	7,984	2,634

*Volume Number of Industry Report

TABLE 4 (continued)

**Assumes East Coast Refinery model applied nationally

***Includes credit of 37 x 10^6 lb SO_2 attributed to energy saved in dry quenching and BOP off gas collection.

****Credit for steam raised: see coverage on fertilizers in Section 3.

TABLE 5. ESTIMATED RANGE IN CONTROLLED SO_x EMISSIONS IN 1989 FOR NEW PROCESSES LIKELY TO BE IMPLEMENTED

Commodity (vol no)*	Likely types of processes to be implemented in new plants	Calculated range in annual SO_x emissions for new plant capacity-1989 (10^6lb/yr)
Steel (III)	Coke oven, blast furnace, BOP****,***	132-138
Petroleum (IV)	Hydrocracking, flexicoking, etc.	308-803*****
Kraft pulp (V)	Kraft, Rapson, alkaline-oxygen	59-844
Newsprint pulp (V)	RMP, TMP, De-inking	12-42
Olefins (VI)	Naphtha, gas oil	102-361
Ammonia (VII)	Heavy fuel oil, coal	21-31
Alumina** (VIII)	Bayer, leaching domestic clays	36-663
Aluminum** (VIII)	Hall-Heroult, aluminum chloride	966-1050
Textiles, knit(IX)	Advanced aqueous, solvent	1-1
Textiles, woven (IX)	Advanced aqueous	9-9
Cement (X)	Preheaters, coal firing, etc.	134-516
Flat glass (XI)	Regenerative furnaces, preheaters, electric furnaces	12-129
Chlor-alkali (XII)	Dimensionally stable anodes, new membranes	424-472
Phosphoric acid: detergent grade (XIII)	Wet acid cleanup	8-8

TABLE 5 (continued)

Commodity (vol no)*	Likely types of processes to be implemented in new plants	Calculated range in annual SO_x emissions for new plant capacity-1989 (10^6 lb/yr)
Copper (XIV)	Oxygen or flash processes***	152-152
Fertilizers-Nitric Acid (XV)	Various NO_x control technologies	(4)-383
TOTAL		2,372-5,602

*Volume Number of Industry Report

**A significant fraction of the incremental U.S. demand is expected to be imported.

***In addition, electric furnaces are expected to be installed based at least partially on scrap.

****With collection of CO from BOF's.

*****Base Case Gulf Coast Refinery model applied nationally.

result in significantly higher SO_x emissions than a Bayer plant based on natural gas, as described in the Alumina/Aluminum Industry report. Although the estimated change in emissions listed in Table 2 was based on incremental capacity from 1974 to 1989 only, in some cases an alternative process, or a process modification, may replace existing capacity. For example, in the aluminum industry, refractory hard metal cathodes may be installed in existing Hall Heroult cells. The application of alternative processes to existing plant capacity will increase the potential effect on SO_x emissions, compared to the estimated effect shown in Table 2. Further perspectives in each of these industry sectors with descriptions of the processes can be obtained from the individual industry sector reports (Volumes III through XV).

R&D AREAS

The following areas of potential R&D for industry, government, or other institutions have been identified with regard to SO_x emissions from the new technologies investigated:

SO_x Related

- Better definition of the environmental, health, and ecological impacts of SO_x emissions with respect to obtaining more quantitative knowledge for establishing appropriate emission regulations.

- In going from gas to oil to coal, increased SO_x emissions may be expected. Therefore, it would be desirable to promote coal-cleaning methods to remove SO_x, coal gasification with SO_x control, and flue gas desulfurization techniques which would help to minimize the dispersal of SO_x and mitigate the SO_x emission problems.

- Promote process alternatives aimed at reducing energy requirements. For a fuel containing a fixed amount of sulfur, SO_x emissions are in direct proportion to the energy consumption and, therefore, reduction in energy consumption will result in lower SO_x emissions. Examples of such potential energy-conserving processes include:

    a) Rapson, alkaline/oxygen and de-inking technologies in the pulp sector;

    b) advanced aqueous or solvent processes in textiles;

    c) CO collection from basic oxygen furnaces;

    d) aluminum production by refractory metal cathodes or by the aluminum chloride (Alcoa) electrolysis route;

e) phosphoric acid (wet acid grade) by the strong acid process;

f) detergent grade phosphoric acid by the chemical clean-up of wet acid; and

g) flotation of copper values from copper smelting slags.

In addition, similar energy conservation and SO_x reduction are achieved by the generic technologies of solid preheating (e.g., in glassmaking, or flash calcining in cement) or use of oxygen (e.g., flash smelting in copper, or the Mitsubishi and Noranda oxygen-based processes).

Process-Related

Cement--

- Develop and implement a comparative test program at a number of cement plants with clinkering facilities employing long-rotary-kiln, suspension preheater, or flash-calciner processes in which coal is burned as the fuel. Coal of various sulfur levels should be tested to determine the effect on operation of the level and nature of sulfur in gas, dust, and clinker. The benefits which derive from the physical and/or chemical cleaning of coal to reduce pyritic sulfur levels in coal for cement manufacturing should also be quantified.

- Develop and implement a commercial-scale test program on one or more flash-calciner-equipped rotary-kiln, cement-making facilities to characterize SO_x emissions. Of particular interest would be the emissions from operating with a bypass of a considerable amount of the combustion gases to eliminate alkalies.

Olefins--

- The olefins industry can benefit from additional research on the removal of sulfur from the cracked gas stream. This stream contains hydrogen sulfide, some carbonyl sulfide, and varying percentages of diolefins and other reactive compounds which tend to foul the acid-gas-removal system. This problem is now being handled by depropanizing the cracked-gas stream before acid gas is removed by scrubbing with diethanolamine. A method for removing the sulfur compounds and acid gases from the cracked-gas stream in the presence of diolefins (i.e., before the depropanizer) would be of significant economic benefit to the olefin producers.

- Naphtha and atmospheric gas oil feedstocks produce significant quantities of byproduct pyrolysis fuel oil. If the

feedstock material to the olefins plant has a sulfur content above a certain concentration, the byproduct pyrolysis fuel oil has sulfur levels too high for its environmentally acceptable use as a fuel without flue gas desulfurization. These byproduct fuel oils also contain substantial amounts of unsaturates as well as other reactive materials which tend to polymerize and form gums on handling. These present problems when attempting to desulfurize the oils. It would be desirable to develop an economically attractive process for desulfurizing the pyrolysis fuel oil to a level where it would be environmentally acceptable as a fuel. At present, most olefin producers limit the sulfur content of their feedstock to circumvent this problem. However, this limitation severely restricts their choice of feedstocks.

Aluminum--

- Consider materials research in the field of producing titanium diboride cathodes suitable in quality to permit long operating life in the Hall Heroult cell. This development would have an effect on energy savings in the existing aluminum plants, thus reducing SO_x emissions at the power boiler.

Pulp and Paper--

- The alkaline oxygen process would alleviate the SO_x pollution problems presently associated with the major alternative manufacturing method--namely, kraft pulping and bleaching. Evaluation of this process and process emissions is desirable.

- The de-inking of old news for the manufacture of newsprint presents an opportunity to save energy and reduce SO_x emissions accompanying the pulping of an equivalent amount of virgin feedstock. Broader commercial application should be supported, because it also could reduce the amount of municipal solid waste.

Glass--

- A proven system to control glass furnace emissions of SO_x and particulates must be developed if cost-effective pollution control is to be obtained. Such a system is required if any of the coal-related processes is to be utilized. While several systems have been developed, such as a coated fabric filter built by Teller Environmental Systems, (Worcester, Mass.), none has been generally accepted by the glass industry as a proven cost-effective technology.

Copper--

- Methods should be developed for removing impurities (e.g., Bi) from blister copper via modified fire-refining procedures. If impurities can be removed from copper, one-step smelting can be used. This would significantly decrease fugitive SO_2 emissions from smelters.

SECTION 3

PROCESSES AND SO_x EMISSIONS

BASES OF CALCULATIONS

In Volume II (P19) describing the methodology used in this study, we indicated that selected State air emission regulations along with the Federal Government's stationary source performance standards and effluent limitation guidelines were surveyed to:

- establish the most probable limits of air emissions, and
- obtain a perspective of the types of pollution control systems to be considered.

While there are a large number of different regulations for airborne emissions at the State regulatory level, we found that approximately the same type of air pollution control systems would be required, regardless of the State or Federal regulations to be met. Generally, these air Pollution control systems included baghouses, venturi scrubbers, inertial impact devices, and electrostatic precipitators for particulates and chemical based systems for sulfur removal, such as alkaline-based aqueous scrubbing for SO_x.

In this Section, SO_x emissions from the process industries (Volumes III through XV) and specific control methods are reviewed. There are two general sources of emissions: the processes themselves and power boilers used for generation of steam and/or electricity. While emissions from the power boiler generally were not considered in the original study, they are included in the present analysis to show the net change in emissions resulting from a process change. Both on-site power boilers and electric utility power boilers are included.

It was found to be important to include power boilers in order to make meaningful comparisons on SO_2 emissions between the base case and alternative processes.

Power boilers are assumed to burn coal containing 3.5% sulfur, and the uncontrolled SO_x emissions are estimated at 5.54 lb of $SO_x/10^6$ Btu (12,000 Btu/lb of coal), or 0.058 lb of SO_x/kWh (based on an average requirement of 10,500 Btu to generate 1 kWh). The uncontrolled SO_x emissions assume 95% of the sulfur in the coal appearing as SO_x in the flue gas largely as SO_2 with only 1-3% as SO_3. The controlled emissions from new plants are assumed to meet the new source performance standard (NSPS) of 1.2 lb of $SO_x/10^6$ Btu, equivalent to about 0.0126 lb of SO_x/kWh. The SO_x emissions from the base case process and process alternatives

are described and summarized for each industry. The SO_x emission factors are estimated, and the effect of these factors on the incremental production from 1974 to 1989 is calculated.

SO_x CONTROL METHODS

Control methods are limited to point sources only and fugitive emissions are not discussed. Since SO_x control methods have been well discussed in the literature, such methods are not described in detail here but are only listed.

Uncontrolled SO_x emissions result from the sulfur present in the fuel and in the feedstock which upon combustion results in SO_x air emissions from high-temperature processes. The control technology for reducing emissions containing sulfur compounds are:

1) reduction of sulfur in the fuel and feedstock;

2) process modifications to prevent escape of sulfur compounds to the atmosphere; and

3) removal of sulfur compounds in the tail gas before it is exhausted to the atmosphere.

Other methods include use of tall stacks and controlling the sulfur compounds concentration in the vicinity of the source. These methods do not reduce the emissions of sulfur compounds to the atmosphere, but are aimed at dispersing the emissions to the atmosphere and at using production curtailment to control ground-level pollutant concentrations. The production curtailment method, used when adverse weather conditions prevail, has been referred to as a "supplementary control system (SCS)," when it is based on the monitoring of sulfur compound concentration at ground level at various sites in the areas surrounding the source, knowledge of which is used to control the production rate.

Reduction of Sulfur Compounds in Feed Materials and Fuel

Sulfur emissions from a process may be reduced by using feed materials and fuel having lower sulfur or content, or by reducing sulfur content in such materials before they are used. The first alternative is not available in all cases, because of the limited supply of materials. Reducing the sulfur content of feed materials and fuel is widely practiced for oil and, to limited extent, for coal.

The applicability of desulfurization of oil in the petroleum industry is determined principally by the characteristics of the oils to be processed and the end-product sulfur specification. Sulfur removal of 90+ % is technically feasible for most oil stocks. The important feedstock properties with respect to influence on the desulfurization of oil are: organometallic compounds (principally nickel and vanadium)

and the asphaltene content of the feedstock. Lower organometallic compounds and asphaltenes are desirable for desulfurization.

The desulfurization of coal is practiced to a lesser extent. Sulfur removal has been in the range of 10-50%. Part of the fuel value of the coal is lost in the process and the loss increases with increased sulfur removal. However, the heating value per ton of cleaned coal may actually rise, especially if some inert materials are simultaneously removed.

Process Modifications to Prevent Escape of Sulfur Compounds in Air Emissions

This method of emission reduction has been applied, to a limited extent, to coal combustion. An alkali such as limestone is added with the coal to the boiler. The limestone reacts with sulfur to form calcium-sulfur salts, which are removed along with the bottom ash. Limestone may also be used to remove sulfur compounds in the generation of gas from coal. A detailed description of this process is given in the discussion of the glass industry found later in this Section.

In some cases, alkali materials, present in the process, help to reduce SO_x emissions. For example, in cement kilns only a fraction of the sulfur present in the feedstock and fuel appears in the flue gas, since the remainder is removed by alkaline particles in the kiln feed.

Removal of Sulfur Compounds from Process Gaseous Emissions

The sulfur compounds in tail gas are present as reduced sulfur compounds or as sulfur oxides. Reduced sulfur compounds, such as hydrogen sulfide, usually have associated odors and, therefore, their emissions are more obnoxious than those of the sulfur oxides. The SO_x in the exhaust gas is generally present as SO_2, except in some cases (such as in glass manufacture) where sulfur emissions are generated from sulfates in the raw materials and result in SO_3 emissions. SO_3 also forms because of oxidation of SO_2 and, similarly, SO_2 may form because of reduction of SO_3.

The SO_3 emissions are difficult to control because the SO_3 is generally present in the form of submicronic mist at the operating temperature of the pollution control equipment. As a result, a very efficient de-mister is required for control.

In the pulp and paper mills, the sulfur compounds are present in reduced form in combination with hydrogen or organic compounds. The control method used involves incineration of the sulfur compounds to convert to sulfur oxides often followed by a pollution control device used to remove the SO_x.

In the petroleum industry, the sulfur compounds are present as COS, H_2S, etc. The gases are removed in an acid gas treatment system for

process requirments. The acid gases are removed by amine absorption or caustic scrubbing. The concentrated gases from the regeneration step of systems, such as amine absorption, are treated in the Claus plants, followed by a tail gas cleanup system, such as the Stretford process. In this way, the sulfur compounds are converted to elemental sulfur. If the volume of the gas stream is small, the Stretford process may be used directly to remove sulfur compounds after the acid gas has been removed.

There are several methods available for removing SO_2 from flue gas. At low concentration (less than 1-2% SO_2) and at low gas-flow rates, alkaline scrubbing may be used to control SO_2 emissions. At low concentrations (less than 0.5% SO_2) and at high gas-flow rates, such as from power boilers, flue gas desulfurization methods (FGD) are used. Depending on the product stream, these methods are classified as follows:

- Waste salt process,
- Concentrated SO_2 process,
- Direct sulfuric acid process, and
- Elemental sulfur process.

For processes that generate concentrated emissions (more than 4-6% SO_2) and large-volume gas streams (such as copper smelting), sulfuric acid plants are used to control the SO_2 emissions.

The SO_x emissions may also be removed by dry processes, as in bag filters, if a coat of alkaline material is present. In cement kilns, bag filters are used to control particulate emissions and, because of the alkaline nature of the particles, a significant fraction of the SO_2 is removed. In some systems, such as in controlling the emissions from glass furnaces, alkaline material is introduced upstream of the bag filters to control SO_x emissions.

PETROLEUM REFINING

Base Case Process - 1985 Refinery

A description of the petroleum refining industry is presented in Volume IV, page 9. In assessing the impact of process changes in the refining industry, a 1985 refinery configuration was used as a base case. The reasons for using this approach are given in Volume IV, page 22. Three configurations were selected to represent the local conditions: the East, Gulf, and West Coasts. Results of our analyses are given in Table 6.

TABLE 6. ESTIMATED SO_x EMISSION FACTORS - PETROLEUM REFINING INDUSTRY

Process	Emission factor* - no control ($lb/10^9$ Btu of refinery output)			Emission factor* - with control ($lb/10^9$ Btu of refinery output)			Control efficiency
	Process	Power boiler	Total	Process	Power boiler	Total	%
Base case: East Coast refinery	84	80	164	84	17	101	38
• Direct combustion of asphalt in process heaters and boilers	360	87	447	93	19	112	75
• Flexicoking	364	80	444	90	17	107	76
Base case: Gulf Coast refinery	31	46	77	31	10	41	47
• Onsite electric power by combustion of asphalt	31	23	54	31	10	41	24
Base case: West Coast refinery	74	55	129	74	12	86	33
• Hydrocracking of heavy bottoms	167	63	230	83	14	97	58
• High-purity hydrogen production via partial oxidation of asphalt	119	59	178	74	13	87	51

*Emissions reported as lb $SO_2/10^9$ Btu of refinery output.

East Coast Refinery

Base Case Process--

The base case East Coast refinery is described in Volume IV, page 23. The energy intake in this refinery (in terms of crude oil, fuel oil, steam, and electricity) is 1.31×10^{12} Btu/day and production is equivalent to 1.19×10^{12} Btu/day (Vol. IV, page 35).

The major airborne pollutants emitted by refineries have been previously identified in Volume IV, page 24. The emission factors summarized in EPA's "Compilation of Air Emission Factors" (1973) were used to determine SO_x emissions from the base case refinery. The SO_x emissions are: 45,200 lb SO_x/day from combustion sources (heaters, oil-fired boilers); 52,800 lb SO_x/day from fluid catalytic crackers; and 2,200 lb SO_x/day from the Claus plant. Uncontrolled emissions of 100,280 lb SO_x/day are equivalent to an emission factor of 84 lb $SO_x/10^9$ Btu of refinery output. The emissions from the combustion sources and fluid catalytic crackers are not controlled. Sulfur emissions from the Claus plant* are based on 99.5% recovery of the sulfur in the acid gas.

Purchased steam and electricity in the base case refinery are equivalent to 8.2×10^9 Btu/day and 8.9×10^9 Btu/day, respectively. The estimated emissions from the associated coal-fired power boiler are 94,700 lb SO_x/day, based on no control, and 20,500 lb SO_x/day, assuming control to meet the New Source Performance Standard (NSPS). The estimated emissions are equivalent to 79.8 lb $SO_x/10^9$ Btu of refinery output, based on no control, and 17.3 lb $SO_x/10^9$ Btu of refinery output, based on control to meet the NSPS resulting in total emissions of 101 lb $SO_x/10^9$ Btu, as shown in Table 6.

Process Option 1 - Direct Combustion of Asphalt in Process Heaters and Boilers--

A detailed description of this alternative appears in Volume IV, page 32. Utilizating asphalt for combustion is intended primarily to upgrade the overall form value of refinery products rather than to actually increase the overall thermal efficiency within the refinery. Part of the refinery gas (36.6%) and all of the fuel oil are displaced by asphalt. The energy balances for the base case process and the alternative are summarized in Volume IV, page 35. In the alternative process, SO_x emissions are increased because of the increased sulfur in the asphalt.

The emissions from the asphalt combustion are 15,395 lb SO_x/hr (Volume IV, page 38). The emissions from the combustion sources in the base case process are eliminated in this alternative, because oil is not used for combustion. Thus, the total refinery emissions are 425,000 lb SO_x/day, equivalent to about 360 lb $SO_x/10^9$ Btu of refinery output.

*For discussion, see Vol. IV, p 152.

The emissions from the asphalt combustion may be controlled by an add-on FGD system. If the SO_x removal efficiency is 85% (Volume IV, page), the emissions from the combustion sources will be reduced to an estimated value of 55,400 lb SO_x/day. The total emissions are estimated at 110,400 lb SO_x/day, equivalent to 93 lb $SO_x/10^9$ Btu of refinery output, as shown in Table 6.

Purchased steam and electricity are 9.7×10^9 Btu/day and 8.9×10^9 Btu/day, respectively (Volume IV, page 35). Estimated emissions from the power boiler are 87 lb $SO_x/10^9$ Btu of refinery output, based on no control, and 19 lb $SO_x/10^9$ Btu of refinery output, based on control to meet the NSPS. Thus, combining these figures results in about an 11% increase in SO_x emissions compared with the base case, as shown in Table 6 and 7.

Process Option 2 - Flexicoking--

Flexicoking is the combination of fluid coking with coke gasification. Although fluid coking is a commercially available technology, there are no commercially operating flexicokers. A detailed process description is given in Volume IV, page 52, with emissions discussed on page 59.

The major air pollution problem associated with the Flexicoking process is in controlling sulfur in the streams of fuel gas (light hydrocarbons containing H_2S) and flexigas (a low-Btu fuel gas containing N_2, CO, CO_2, H_2, and sulfur, and its compounds).

The sulfur in the fuel gas is removed using an amine scrubbing system, and the exhaust of that scrubbing system is sent to the refinery Claus plant. The hydrogen sulfide in the low-Btu flexigas is too low in concentration to be economically scrubbed out, and, therefore, this process comes with an integral Stretford unit* for sulfur removal. The sulfur concentration in the product flexigas is approximately 170 ppm, which is within allowable standards for combustion without sulfur control.

The emissions having sulfur compounds are 2,920 lb SO_x/day from the combustion of flexigas and 159,580 lb sulfur/day, in the acid gas stream. The total emissions from the refinery are equivalent to 364 lb $SO_x/10^9$ Btu of refinery output. If the sulfur emissions in the acid gas stream are controlled, the total emissions from the refinery are reduced to an estimated value of 90 lb $SO_x/10^9$ Btu of refinery output, as shown in Table 6.

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*Some additional background on the Stretford process is found in Volume XI, p 38, "Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Petroleum Refining Industry Report"

TABLE 7. ESTIMATED SO_x EMISSIONS - PETROLEUM REFINING INDUSTRY

Process	Emission factor ($lb\ SO_x/10^9$ Btu of refinery output)			Change in emission factor	SO_x Emissions (10^6 lb/yr)	
	Process	Power boiler	Total		1974	1989-1974*
Base case: East Coast refinery	84	17	101	--	3,030**	758
• Direct combustion of asphalt in process heaters and boilers	93	19	112	+11	--	840
• Flexicoking	90	17	107	+6	--	803
Base case: Gulf Coast refinery**	31	10	41	--	1,230**	308
• Onsite electric power by combustion of vacuum bottoms	31	10	41	0	--	308
Base case: West Coast refinery**	74	12	86	--	2,580**	645
• Hydrocracking of heavy bottoms	83	14	97	+11	--	728
• High purity hydrogen production via partial oxidation of asphalt	74	13	87	+1	--	653

TABLE 7 (continued)

*Based on incremental national production from 1974 to 1989 equal to 7.5 quads (7.5×10^{15} Btu) multiplied by emission factor asssuming no retirement of existing facilities.

**Estimated 1974 emissions, based on the total emission factors and production of 30 quads are $3,030 \times 10^6$ lbs, $1,230 \times 10^6$ lbs and $2,580 \times 10^6$ lbs for East Coast, Gulf Coast and West Coast models, respectively.

The emissions from the power boiler are comparable to those in the base case process, i.e., about 80 lb SO_x/10^9 Btu of refinery output, based on no control, and 17 lb SO_x/10^9 Btu of refinery output, based on control to meet the NSPS. Total SO_x emissions thus increase by about 6% as shown in Tables 6 and 7.

Gulf Coast Refinery

Base Case Process--

The base case refinery configuration in the year 1985, located on the Gulf Coast is described in Volume IV, page 23. Total energy input in the base case refinery is 1,358 x 10^9 Btu/day and production is equivalent to 1,197 x 10^9 Btu/day. SO_x emissions from this base case process were developed in a manner similar to that for the East Coast refinery using oil-fired boilers.

The emissions include 27,600 lb SO_x/day from combustion sources; 8,400 lb SO_x/day from fluid catalytic crackers and 680 lb SO_x/day from the Claus plant. The total emissions of 36,680 lb SO_x/day (Volume IV, page 25) are equivalent to 31 lb SO_x/10^9 Btu of refinery output. Sulfur emissions from the Claus plant are based on 99.5% recovery of the sulfur in the acid gas.

Based on electricity consumption equivalent to 9.2 x 10^9 Btu/day and steam consumption equivalent to 0.7 x 10^9 Btu/day (Volume IV, page 70), the estimated emissions from the power boiler are 46 lb SO_x/10^9 Btu, based on no control, and 10 lb SO_x/10^9 Btu, based on control to meet the NSPS, resulting in total discharges of 41 lb SO_x/10^9 Btu.

Process Option - On-site Electric Power by Combustion of Vacuum Bottoms--

In this process alternative, electric power is generated within the refinery rather than purchased from a local electric utility. The fuel is assumed to be asphalt. A simplified flow sheet for this alternative is shown in Volume IV, page 69.

Generation of electric power within the refinery neither conserves energy nor consumes more energy than when power is purchased, assuming that the internal and external power plants would operate at the same efficiencies. In effect, the form value of the asphalt is upgraded to a higher form value of electric power for refinery use. The design capacity of the generator, as shown in Volume IV, page 77, is 36.5 megawatts.

This process alternative will result in increased on-site SO_x emissions. SO_x emissions from the on-site power boiler are 27,456 lb SO_x/day (Volume IV, page 73), equivalent to 23 lb SO_x/10^9 Btu of refinery products. The costs of sulfur control for on-site electric power generation is shown in Volume IV, page 76. If the emissions are

controlled to meet the NSPS, the resulting SO_x emissions will be about 10 lb $SO_x/10^9$ Btu of refinery output.

West Coast Refinery

Base Case Process--

The base case refinery configuration in the year 1985, located on the West Coast, is described in Volume IV, page 23. Total energy input in the base case refinery is $1,009 \times 10^9$ Btu/day and production is equivalent to 950×10^9 Btu/day. SO_x emissions from the base case process were developed in a manner similar to that for the East Coast refinery using oil-fired boilers.

The emissions include 58,800 lb SO_x/day from combustion sources; 7,600 lb SO_x/day from fluid catalytic crackers; and 3,680 lb SO_x/day from the Claus plant. The total emissions of 70,080 lb SO_x/day (Volume IV, page 26) are equivalent to 74 lb $SO_x/10^9$ Btu of refinery output. Sulfur emissions from the Claus plant are based on 99.5% recovery of the sulfur in the acid gas.

Based on electricity consumption equivalent to 9.5×10^9 Btu/day (Volume IV, page 46), the estimated emissions from the power boiler are 55 lb $SO_x/10^9$ Btu of refinery output, based on no control, and 12 lb $SO_x/10^9$ Btu based on control, to meet the NSPS, resulting in total discharges of 86 lb $SO_x/10^9$ Btu.

Process Option 1 - Hydrocracking of Heavy Bottoms--

In this option, asphalt is used as a feedstock for a hydrocracking process such as H-Oil or Isomax in which the heavy bottoms are converted to lighter fuel oils and gaseous products. The H-Oil process was chosen to exemplify a heavy-ends hydrocracking process. A detailed description of the process is given in Volume IV, page 43. The pollutants of concern in this option are H_2S, generated in the gaseous products, and SO_2, generated from the combustion of a small amount of asphalt. The gases from the H-Oil reactor will pass through an amine scrubbing system to remove H_2S and CO_2. These are sent to a Claus plant for sulfur control. Since a refinery normally would have a Claus plant, the cost of control for this option is only the incremental cost required to expand the Claus plant to handle the additional sulfur load (Volume IV, page 152).

In addition to the sulfur control costs for hydrotreating, the equivalent of 900 BPD of asphalt also has to be burned in the process heaters to free up refinery gas which can be used to generate the additional hydrogen needed for the hydrotreater. Since the asphalt has a sulfur content higher than the allowed maximum uncontrolled sulfur content of a fuel, flue gas desulfurization will be required. If all of the asphalt were burned in a single process heater, the size would be approximately 240×10^6 Btu/hr.

The incremental uncontrolled emissions include 715 lb SO_x/day from purge gas, 54,530 lb S/day from acid gas stream, and 12,748 lb SO_x per day from asphalt combustion (Volume IV, page 48). Total emissions from the refinery are about 192,600 lb SO_x/day, equivalent to 167 lb $SO_x/10^9$ Btu of refinery output.

If the sulfur emissions from the tail gas are controlled by the Claus plant and the emissions from the asphalt combustion are controlled by the wet scrubber, the incremental emissions will be reduced to an estimated value of 8,170 lb SO_x/day (to meet EPA standards). Therefore, the total estimated controlled emissions from the refinery are about 83 lb $SO_x/10^9$ Btu of refinery output.

Based on electricity consumption of 10.8×10^9 Btu/day (Volume IV, page 46), the estimated emissions from the power boiler are 63 lb $SO_x/10^9$ Btu of refinery output if no control is provided, and 14 lb $SO_x/10^9$ Btu of refinery output if the emissions are controlled to meet the NSPS. The total SO_x emissions will then be 83 plus 14 or 97 lb/10^9 Btu of output; an increase of 13%.

Process Option 2 - High-Purity Hydrogen Production via Partial Oxidation of Asphalt--

This alternative is based on the production of high-purity hydrogen for hydrotreating from vacuum bottoms, using a partial oxidation process. The feedstock freed up by this approach would then be available for sale outside the refinery in the form of pipeline gas or naphtha. A detailed process description is given in Volume IV, page 78.

The major emission associated with this process change is the sulfur removed from the raw syngas in the form of H_2S. This is removed from the gas using an amine scrubber system. The exhaust from the amine regenerator, which contains the sulfur as well as CO_2, is sent to a Claus plant for sulfur recovery and air pollution control. Several states have emission standards regulating tailgas for sulfur recovery plants so that tailgas cleanup will be required to limit emissions from the plant to 250 ppm or less. The incremental uncontrolled emissions are 21,200 lb of S/hr, equivalent to 45 lb of $SO_x/10^9$ Btu of refinery output. If the emissions are controlled, the additional emissions are estimated to be equivalent to 0.2 lb $SO_x/10^9$ Btu of refinery output.

The emissions from the power boiler (coal-fired) are estimated at 59 lb $SO_x/10^9$ Btu of refinery output, based on no control, and 13 lb $SO_x/10^9$ Btu of refinery output, based on control to meet the NSPS. Tables 6 and 7 show that SO_x emissions are only 1% higher than those for the base case process.

Summary

Table 6 shows that uncontrolled emissions are increased in all alternatives, except for the case of on-site generation of electric

power by combustion of asphalt. The sulfur content in the asphalt is lower than that in the coal burned in the power boiler.

The emission control methods include removal of reduced sulfur in acid gas cleaning followed by the Claus and Stretford plants, and flue gas desulfurization. As shown in Table 6, overall control efficiency varies from 24 to 76 percent. Also, the controlled emissions in the alternative processes are comparable or higher than those in the corresponding base case process. Based on the assumption that each process option is considered individually for application in 100% of refinery expansion, the controlled SO_x emissions from refinery industry are summarized in Table 7. Examination of Table 2 shows that even small percentage changes in the petroleum industry can have significant national impact.

CEMENT

Base Case Process - Long Rotary Kiln

The production of finished cement from raw materials involves four steps: crushing, grinding, clinkering, and finish grinding. From a materials viewpoint hydraulic cement is a powder made by heating lime, silica, alumina, iron oxide, and magnesia together in a kiln and then pulverizing the product. The base case process selected for the cement industry was the long rotary kiln with dry grinding. In the dry cement process, grinding is performed dry, very much like wet grinding, except that no water is added and the material is ground at 1% moisture content or less. A detailed description of the process is given in Volume X, page 84.

The base case process is based on natural gas or oil as fuel. However, the emissions are estimated using natural gas as a fuel in the cement kiln since more natural gas than oil was used in 1974 in the cement industry (Volume X, page 92). Very little sulfur is present in the natural gas, so all the emissions result from sulfur present in the raw materials. The uncontrolled emission factor is 10.2 lb SO_x/ton of cement as reported in "Compilation of Air Emission Factors" (EPA, 1973). In addition, gaseous emissions from the combustion of high sulfur fuel in the kiln are usually not sufficient to create significant air pollution problems. Most of the sulfur dioxide formed from the sulfur in the fuel is recovered as it combines with the alkalies and also with the lime when the alkali fume is low.

Usually bag filters are used to control particulate emissions from the cement kilns (Volume X, page 101). With bag filters, approximately 50% of the SO_x is removed by passage through the alkaline particulate filter cake. Other control methods include reduction of sulfur in the feed and fuel to the kiln.

In addition to the process emissions, electricity consumed in the

plant will result in emissions at the power boiler. The electricity consumed in the long kiln is equivalent to 1.61×10^6 Btu/ton of cement resulting in estimated uncontrolled emissions of 8.9 lb SO_x/ton of cement. If the emissions are controlled to meet the NSPS, the emissions will be reduced to an estimated value of 1.9 lb SO_x/ton of cement. Consequently, the total controlled SO_x emissions will be 7.0 lb/ton.

Process Option 1 - Suspension Preheater

The suspension preheater is a modification of, or addition to, the cement rotary kiln. It is attached to the raw feed inlet end of the kiln, totally replacing the preheating zone. The suspension preheater preheats the raw material and also accomplishes a considerable amount of raw material calcination. Typical suspension preheaters heat cold raw feed to approximately 1,400°F and accomplish 30-40% of the total calcination or thermal decomposition of the calcium carbonate, the main component of the raw feed. Consequently, with the suspension preheater, the rotary kiln receives hot and partially calcined raw material. There are several variations on the suspension preheater (described in Volume X, page 19).

Raw material which has been partially calcined is highly reactive with sulfur dioxide and oxygen, forming calcium sulfite and sulfate. Any SO_x which might form in the combustion gases in a rotary kiln, even using high-sulfur coal as fuel, contacts the raw material so intimately that the use of a suspension preheater system should not present any sulfur dioxide emission problems. However, no quantitative data are available, so emissions cannot be estimated.

The electricity consumption is reduced to 1.32×10^6 Btu/ton of cement, so the estimated emissions from the power boiler are 7.3 lb SO_x/ton of cement, based on no control and 1.6 lb SO_x/ton of cement based on control to meet the NSPS. Overall, some reduction on SO_x emissions can be expected.

Process Option 2 - Flash Calciner

Although designs of flash calcining systems vary, the main feature which characterizes the flash calciner rotary kiln is the flash calcining vessel added between the rotary kiln and the suspension preheater. A detailed process description is given in Volume X, page 34.

The flash calciner arrangement (described in Volume X, page 23) requires a considerable amount of excess combustion air in burning the fuel in the rotary kiln so that enough air is present in the combustion gases leaving the kiln to permit combustion of the fuel in the flash calcining vessel.

By the time the combustion gases exit to the atmosphere, essentially all of the SO_x should be absorbed and reacted with the raw feed.

However, any gases which might be bypassed could be different in SO_x content from suspension preheater bypass gases because the raw feed entering the flash calciner kiln is almost completely calcined, and also has a significantly lower kiln residence than in a suspension preheater. However, no quantitative data are available, so the emissions cannot be estimated but are thought to be lower than the long kiln.

The electricity consumption is comparable to that in the suspension preheater alternative and therefore the estimated emissions from the power boiler are 7.3 lb SO_x/ton of cement based on no control, and 1.6 lb SO_x/ton of cement based on control to meet the NSPS.

Process Option 3 - Fluidized-Bed Cement Process

The only difference between the fluidized-bed cement process and the conventional process is the high-temperature clinkering step. All of the other steps are essentially identical. A detailed description of the process is given in Volume X, page 40. Comparing the energy consumption in the fluidized bed and in the long kiln (Volume X, page 46), one finds the fuel consumption in the fluidized bed to be about 10% higher. No quantitative data regarding SO_x emissions are available so emissions cannot be estimated but are thought to be lower than in the long kiln.

There is a net recovery of energy in the form of electricity in the fluidized bed process (0.15×10^6 Btu/ton of cement; Volume X, page 46) resulting in a credit (i.e., negative emissions) at the power boiler estimated at 0.83 lb SO_x/ton of cement, based on no control; and 0.18 lb SO_x/ton of cement, based on control to meet the NSPS.

Process Option 4 - Conversion to Coal Fuel from Natural Gas

The process description using coal as a fuel in the cement kiln is described in Volume X, page 60. The use of coal as fuel in the cement kiln will increase the SO_x emissions because there is more sulfur in the coal than in the gas. The reported emission factor is 6.8 lb SO_x/ton of cement per percent sulfur in the coal (EPA, 1973). Therefore, for a 3.5% sulfur coal, emissions are estimated at 23.8 lb SO_x/ton of cement. The total emissions from the cement kiln, due to sulfur in both the feed materials and the fuel, are 34 lb SO_x/ton of cement. Again, if bag filters are used to control particulate emissions, the SO_x emissions are reduced by 50% to 17 lb/ton of cement (EPA, 1973). The emissions from the power boiler are the same as those from the base case process, giving a total controlled SO_x emission of 18.9 lb/ton of cement, a significant 170% increase.

Summary

SO_x control devices are generally not used in the cement industry. However, bag filters used for particulate control can reduce SO_x

emissions by 50% because of the alkaline filter cake. The controlled emission factors are shown in Tables 8 and 9 for the base case and alternative processes.

Controlled emissions from the use of coal as fuel (instead of natural gas) in the long-dry kiln alternative are highest because of the higher sulfur content of the coal. The sulfur in the feed in other processes is lower. Emissions from the fluidized bed should be lowest because of higher SO_x removal in the fluidized bed.

OLEFINS

Ethylene Production

Base Case Process - Ethylene Production Based on Ethane and Propane Cracking--

The base case technology selected for the assessment of the domestic olefin industry was ethane and propane (E-P) cracking. A detailed description of the process of producing ethylene from ethane and propane is given in Volume VI, page 17.

As a basis for calculation, a feedstock containing 10 ppm sulfur is used. During the ethylene cracking process, sulfur is produced in the form of H_2S and COS. These gases and CO_2 (the acid gases) are removed from the compressed cracked gases by a caustic (sodium hydroxide) scrubber (Volume VI, page 103). The liquid effluent from the caustic scrubber is contacted with naphtha to absorb entrained hydrocarbons. The naphtha solution is decanted and then used as a fuel. The water effluent from the naphtha wash is neutralized with sulfuric acid, resulting in the following effects:

- Sulfides, such as Na_2S or NaHS, are replaced by Na_2SO_4. This sulfate can be discharged from the plant as dissolved solids in water effluents unless local conditions prohibit;
- The acid gases are regenerated and must be incinerated to convert H_2S to SO_2 before venting to the atmosphere;
- In the base case process, a feed sulfur concentration of 10 ppm in E-P results in an SO_2 exhaust of about 0.04 lb/ton of ethylene (Volume VI, page 43).

The only other sulfur emission from an E-P cracker occurs during the decoking operation. The quantity of sulfur emitted is very small.

Some SO_x emissions are expected from the fuel used in the power boiler. The electricity consumed is equivalent to 900 Btu/lb of ethylene. The estimated uncontrolled emissions are 9.98 lb SO_x/ton of ethylene and the emissions controlled to meet the NSPS are estimated at 2.13

TABLE 8. ESTIMATED SO_x EMISSION FACTORS - CEMENT INDUSTRY

Process	Emission factor - no control (lb/ton of cement)			Emission factor - with control (lb/ton of cement)			Control Efficiency %
	Process	Power boiler	Total	Process	Power	Total	
Base case:							
Long kiln (natural gas)	10.2	8.9	19.1	5.1	1.9	7.0	63
• Suspension preheater (natural gas)	< 10.2	7.3	< 17.5	< 5.1	1.6	< 6.7	62
• Flash calciner (natural gas)	< 10.2	7.3	< 17.5	< 5.1	1.6	< 6.7	62
• Fluidized bed (natural gas)	< 10.2	-0.8	< 9.4	5.1	-0.2	< 4.9	--
• Coal as fuel instead of gas in long kiln	34	8.9	42.9	17	1.9	18.9	56

TABLE 9. ESTIMATED CONTROLLED SO_x EMISSIONS - CEMENT PRODUCTION

Process	SO_x Emission factor for cement production (lb/ton of cement) Process	Boiler	Total	Change in emission factor	SO_x emissions (10^6 lb/yr) 1974**	1989-1974*
Base case: Long kiln (natural gas)	5.1	1.9	7.0	--	553	191
• Suspension preheater (natural gas)	< 5.1	1.6	< 6.7	-0.3	--	183
• Flash calciner (natural gas)	< 5.1	1.6	< 6.7	-0.3	--	183
• Fluidized bed (natural gas)	< 5.1?	-0.2	< 4.9	∿-2.1	--	∿134
• Coal as fuel instead of gas in long kiln	17	1.9	18.9	+11.9	--	516

*Based on the incremental production of cement from 1974 to 1989 of 27.3×10^6 tons (Table 1) multiplied by total SO_x emission factors; this assumes no retirement of existing facilitites.

**The SO_x emissions in 1974 are based on the emission factor of 7.0 lb SO_2/ton of cement are $7.0 \times 79 \times 10^6 = 553 \times 10^6$ lbs.

lb SO_x/ton of ethylene. The total SO_x emissions are then about 2.2 lb/ton.

The process and boiler emissions are summarized in Table 10. Emissions from alternative processes are also included in the table.

Process Option 1 - Ethylene from the Pyrolysis of Naphtha--

Pyrolysis of naphtha already accounts for 7% of domestic ethylene production and is the predominant technology used in Europe and Japan. This process alternative is described in Volume VI, page 22.

A sulfur concentration of 500 ppm in the naphtha feed was used as a basis for calculation. This is equivalent to 6.1 lb SO_2/ton of ethylene. Sulfur in the feed is later found in the pyrolysis gas (typically 80% of the total sulfur is found in the hydrocarbon fraction containing four carbon molecules or less, e.g., C'_4s and lighter, equivalent to 4.9 lb SO_x/ton of ethylene); in the pyrolysis gasoline (8% of the sulfur equivalent to 0.45 lb SO_x/ton of ethylene); and in the fuel oil (12% of the sulfur equivalent to 0.75 lb SO_x/ton of ethylene).

Two methods of H_2S removal are available: simple caustic scrubging, and regenerative amine scrubbing followed by a caustic wash to remove the final traces of sulfur and CO_2 . In the Petroleum Refining Industry Report (Vol. IV) a simple caustic scrubbing system was chosen since such a system normally is used until sulfur levels in the C_4 fraction of the pyrolysis gases exceed 600 ppm.

All the fuel oil produced in the olefin plant is consumed in heaters, so sulfur in the fuel oil will result in an estimated uncontrolled emission of 0.75 lb SO_x/ton of ethylene; these are not currently controlled.

SO_x emissions are expected from the fuel burned in the power boiler. The electricity consumed is equivalent to 1,100 Btu/lb of ethylene. The estimated uncontrolled emissions are 12.2 lb SO_x/ton of ethylene and the emissions controlled to meet the NSPS are estimated at 2.6 lb SO_x/ton of ethylene. The total controlled SO_x emissions are then 3.6 lb/ton of ethylene; an increase of 64% over the base case.

Process Option 2 - Ethylene From the Pyrolysis of Gas-Oil--

Several plants now being constructed will use gas-oil as feed. The design of such plants is well established at the commercial level and the practice is clearly going to become common as ethylene producers move to assure themselves of some flexibility in their choice of feedstock. A process description for ethylene production based on gas-oil is given in Volume VI, page 27.

A sulfur concentration of 2,000 ppm in the feedstock (equivalent to 32.2 lb SO_2/ton of ethylene) was used as the basis for calculation.

TABLE 10. SULFUR DISTRIBUTION AND ESTIMATED SO_2 EMISSION FACTORS - OLEFIN INDUSTRY
(LB SO_2/ TON ETHYLENE)

	Base case Ethane-Propane	Naphtha	Gas oil
Feed*	0.03	6.1	32.2
Distribution			
Acid gas**	0.03	4.9	8.7
Fuel oil	--	0.75	21.0
Gasoline	--	0.45	2.5
Total	0.03	6.1	32.2
Emissions (uncontrolled)			
Acid gas	0.03	4.9	8.7
Heater exhaust***	--	0.75	8.82
Total process	0.03	5.65	17.52
Power boiler	9.98	12.2	16.64
Total	10.0	17.9	34.2
Emissions (controlled)			
Acid gas removal exhuaust	0.03	0.26	0.39
Heater exhaust***	--	0.75	8.82
Total process	0.03	1.01	9.21
Power boiler	2.13	2.6	3.54
Total	2.2	3.6	12.8
Control efficiency, %	78	80	63

*Feed does not include fuel for power boiler.

**Before acid gas recovery (sulfur is present as H_2S and COS, but sulfur weight is calculated on SO_2 basis.)

*** From combustion of fuel oil - 100% of the fuel oil produced is consumed in the naphtha process and 42% of the fuel oil produced is consumed in the gas oil process. These emissions are normally not controlled.

The SO_2 emission problems and control methods in this alternative are identical to those in the ethylene from the pyrolysis of naphtha alternative. The uncontrolled and controlled emissions are shown in Table 10.

As in the base case process, the gas-oil cracker supplies its own fuel needs. This is accomplished by a recycling of all the residue gas and 42% of the fuel oil produced. Thus, estimated uncontrolled emissions from the heaters are 8.82 lb SO_x/ton of ethylene as shown in Table 10.

Additional SO_x emissions are expected from the fuel burned in the power boiler. The electricity consumed is equivalent to 1,500 Btu/lb of ethylene (or 3 million Btu/ton ethylene). The estimated uncontrolled emissions are 16.6 lb SO_x/ton of ethylene and the emissions controlled to meet the NSPS are estimated at 3.54 lb SO_x/ton of ethylene. The total controlled emissions are 12.8 lb/ton of ethylene, a 480% increase over the base case, largely due to heater exhaust emissions.

Long-Term Process Options

The more active development programs in the area of olefin technologies which were not analyzed in depth in the original study include:

- Cracking technology, such as
  - Coil cracking of vacuum gas oil,
  - Hydropyrolysis,
  - Autothermic pyrolysis, and
  - Fluid bed cracking, as well as
- Coal-based technology, such as
  - Plasma arc pyrolysis, and
  - Clean coke process.

Since most of these advanced technologies are being developed and commercialized during a period when environmental regulations are in effect, the developers recognize the need to comply with existing environmental codes and are taking appropriate measures while developing the process. Sulfur is an even more significant problem for these advanced technologies than for the existing technologies, because of the nature and sulfur content of the proposed feedstocks. However, for all, the gaseous sulfur is in the form of hydrogen sulfide, for which an abundance of control technology is available, although some of this technology may require modifications to be effective. For example, Union Carbide has had to do this to reduce the problem of butadiene

polymerization in amine scrubbing systems. Again, the fuel oils and pitch produced as byproducts will present internal use and marketing problems if steps are not taken to reduce their sulfur contents. However, the problems of sulfur content in the byproducts are generally recognized by the developers. Thus, to be acceptable, the commercial versions of the processes must incorporate techniques for coping with this problem.

Summary

The emission factors for the base case process and alternative processes in the olefin industry are summarized in Table 10. The uncontrolled emissions from the alternative processes are significantly higher than those from the base case process. The higher emissions are mainly due to the higher sulfur content in the feedstocks (naphtha and gas oil) and partly due to increased consumption of electricity. The major fraction of the emissions is controlled by add-on control technology. The control efficiency varies from 60 to 80%. The estimated SO_x emissions after control from the olefin industry are summarized in Table 11. Obviously, with the very high growth rate anticipated by this industry (8%/yr), careful attention will have to be given to all forms of potential discharges, including sulfur, and to effective and economical control. As shown in Table 11, use of the heavier gas-oil feedstocks will very dramatically increase the controlled SO_x emissions.

AMMONIA

Base Case Process - Ammonia Production Based on Natural Gas

Ammonia is made by the reaction of nitrogen with hydrogen. All processes manufacturing ammonia utilize air as the source of nitrogen. Natural gas is generally used as the source of hydrogen. The four major operations in manufacturing ammonia are: gas preparation, carbon monoxide conversion, gas purification, and ammonia synthesis. A detailed description of the process is given in Volume VII, page 25.

There are no SO_x emissions from the process. The emissions from a coal-fired power boiler are estimated at 2.6 lb SO_x/ton of ammonia with no control, and 0.6 lb SO_x/ton of ammonia based on control to meet the NSPS. The emissions are based on electricity consumption of 45.5 kWh/ton of ammonia (Volume VII, page 29).

Process Option 1 - Ammonia Production Based on Coal Gasification

Using coal as a feedstock for ammonia production involves freeing the hydrogen that is present in the fuel, and reacting the carbon in the fuel with water vapor to release more hydrogen. A detailed process description is given in Volume VII, page 37, for a hypothetical plant in Southern Illinois using coal with 4.33% sulfur.

TABLE 11. ESTIMATED CONTROLLED SO_x EMISSIONS - OLEFINS INDUSTRY

Process	SO_x Emission factor for olefin production (lb/ton ethylene)				SO_x Emissions (10^6 lb/yr)	
	Process	Power boiler	Total	Change in emission factor	1974	1989-1974*
Base case:						
E-P process	0.03	2.13	2.2	--	28.6**	62
• Naphtha process	1.01	2.6	3.6	+1.4	--	102
• Gas-oil process	9.21	3.54	12.8	+10.6	--	361

*Based on incremental production from 1974-1989 of 28.2 million tons (Table 1) multiplied by total SO_x emission factor. This assumes no retirement of facilities existing in 1974.

**Estimated 1974 emissions, based on the total emission factor of 2.2 lb SO_x/ton of ethylene, are $2.2 \times 13 \times 10^6 = 28.6 \times 10^6$ lb.

The effluent stream from the CO shift-conversion step contains hydrogen sulfide, carbonyl sulfide, etc. These gases must be removed for process reasons, and a number of different acid gas removal systems may be used. The acid gas may be removed in a Rectisol process (Volume VII, page 42) followed by a Claus conversion plant.

Coal consumption is 1.57 tons per ton of ammonia (Volume VII, page 45). The uncontrolled emissions, based on 4.33% sulfur in Illinois coal, are 136 lb S/ton of ammonia. The controlled emissions from a tail gas cleanup system in the Claus unit are estimated at 0.4 lb SO_x/ton of ammonia (Volume VII, page 61).

The estimated emissions from the power boiler are 9.4 lb SO_x/ton of ammonia with no control, and 2.0 lb SO_x/ton of ammonia, based on control to meet the NSPS, giving a total controlled emission of 2.4 lb SO_x/ton, which is 300% more than from the base case process.

Process Option 2 - Production of Ammonia from Heavy Fuel Oil

The production of ammonia from heavy fuel oil includes reacting fuel oil with oxygen in the presence of steam at a temperature of 2,000°-2,500°F to produce syngas, followed by shift reaction, heat recovery, acid gas removal, final gas purification, compression, and synthesis. An air separation plant is required to produce oxygen and nitrogen. A detailed description of the process is given in Volume VII, page 67.

The air pollution problems in this alternative are similar to those in the production of ammonia from coal. However, the uncontrolled emissions are about two-thirds of those from an alternative process based on coal (Volume VII, page 78). The estimated uncontrolled emissions are 92 lb S/ton of ammonia. The controlled emissions from the tail gas system in the Claus plant are 0.3 lb SO_x/ton of ammonia.

The estimated emissions from the power boiler are 6.0 lb SO_x/ton of ammonia with no control, and 1.3 lb SO_x/ton of ammonia, based on control to meet the NSPS. Thus, the total SO_x discharges are 1.6 lb/ton ammonia or 67% more than from the base case process.

Summary

The SO_x emissions from the base case process and process alternatives are summarized in Table 12. The uncontrolled emissions are significantly higher in the alternative process because of the increase in the sulfur content of the feedstock and increased consumption of electricity. The sulfur emissions may be controlled by both Claus plant and FGD systems. The controlled sulfur emissions from the alternative processes are two to four times those from the base case process, but remain relatively small in comparison to other national problems. The total SO_x emissions for the industry in 1989 would be only 13.2×10^6 lb, using the current process, or 36.2 lb, using the base process, plus

TABLE 12. ESTIMATED CONTROLLED SO_x EMISSIONS - AMMONIA INDUSTRY

Process	SO_x emission factor for ammonia production (lb/ton ammonia)				SO_x Emissions (10^6 lb/yr)	
	Process	Power boiler	Total	Change in emission factor	1974	1989-1974*
Ammonia production based on						
Base case:						
Natural gas	0	0.6	0.6	--	5.5**	7.7
• Coal gasification	0.4	2.0	2.4	+1.8	--	30.7
• Heavy fuel oil	0.3	1.3	1.6	+1.0	--	20.5

*Based on increment in production from 1974-1989 -- 12.8×10^6 ton/yr.

**Estimated 1974 emissions, based on the total emission factor of 0.6 lb SO_x/ton of ammonia, are $0.6 \times 9.2 \times 10^6 = 5.5 \times 10^6$ lb/yr.

the ammonia from coal process for all future expansion ("worst case"). Although this is small on a national basis when compared to current or anticipated coal usage and SO_x generation for power utilities, there may nevertheless be significant regional impacts because of the regional character of the ammonia industry.

ALUMINA AND ALUMINUM

Alumina Production

Base Case Process - Bayer Process for Producing Alumina--

The Bayer process for producing alumina is based on imported bauxite. The process includes digestion of ground bauxite, removal of impurities, precipitation of aluminum trihydrate, treatment of spent liquor to regenerate the caustic, and calcination of aluminum trihydrate to produce pot feed alumina. A detailed description of the process is given in Volume VIII, page 106, based on natural gas use in calcining.

There are no SO_x emissions from the process using natural gas. Estimated SO_x emissions from the power boiler (based on electricity consumption of 275 kWh/ton of alumina) are 16 lb SO_x/ton of alumina, if not controlled, and 3.3 lb SO_x/ton of alumina, if controlled to meet the NSPS.

Process Option 1 - Hydrochloric Acid Ion Exchange Process--

This process includes dehydration of the raw clay, leaching with hydrochloric acid, separation of residue, purification of the solution by amine ion exchange, crystallization of aluminum chloride and decomposition and calcination to obtain alumina. A detailed description of the process is given in Volume VIII, page 22. No commercial plant employing this process has ever been built (Volume VIII, page 27); thus, data for emissions are best estimates, based on natural gas for calcining.

As in the base case process, SO_x emissions are not present in this process. Estimated SO_x emissions from the power boiler are 8 lb SO_x/ton of alumina with no control and 1.7 lb SO_x/ton of alumina, if controlled to meet the NSPS -- a 48% reduction.

Process Option 2 - Nitric Acid Ion Exchange Process--

This process includes calcining the kaolin clay, leaching the calcined clay with hot nitric acid, separating the clay insolubles, removing the iron and other impurities, recovering the alumina by hydrolysis, recovering the nitric acid, and calcining to obtain alumina.

In this process, coal and oil are used as fuel. SO_x is present in several waste gas streams (Volume VIII, page 38) and in the flue gas from the combustion processes. Most of the coal is used for calcination.

Part of the SO_x will be removed in the alkaline dust present in the kiln. It is expected that SO_x emissions may be comparable to those from the coal combustion in the cement kiln. If coal containing 3.5% sulfur is used in the cement kiln, the SO_x emissions will be 23.8 lb SO_x, based on the emission factor reported in "Compilation of Air Pollution Emission Factors" (EPA, 1973). The fuel consumption in the cement kiln is about 4.6×10^6 Btu/ton of cement (Volume X, page 46). The coal consumption in the nitric acid process is 24×10^6 Btu/ton of alumina. Therefore, the estimated uncontrolled SO_x emissions are 120 lb SO_x/ton of alumina.

In the operation of a cement kiln, about 50% of the SO_x emissions are removed in the particulate collection device. Comparable collection efficiency may be expected in this alternative. The estimated emissions from the particulate collection device will be 60 lb SO_x/ton of alumina.

The emissions from the power boiler are comparable to those in the hydrochloric acid ion-exchange process alternative, about 8 lb SO_x/ton of alumina, if not controlled, and 1.7 lb SO_x/ton of alumina, if controlled to meet the NSPS. Consequently, at 1.7 lb SO_x/ton, this route will be a significantly larger contributor of SO_x than the conventional bauxite process, largely because of coal use in these calculations.

Process Option 3 - Toth Alumina Process--

This process involves the chlorination of alumina-containing raw materials in the presence of carbon to produce aluminum chloride vapor and other volatile chlorides. These products are subsequently purified to eliminate other metal chlorides and then oxidized to alumina and chlorine for recycle. The details of the process are given in Volume VIII, page 39.

Coal is the only source of sulfur in this process. Coal is used in kilns, chlorinator, etc. The coal consumption in the process is equivalent to 8.45×10^6 Btu/ton of alumina. If all the sulfur from the coal (containing 3.5% sulfur) appears in the flue gas, it will result in an estimated uncontrolled emission of 49 lb SO_x/ton of alumina.

The major sulfur source is the chlorinator. After chlorine is removed, the gas contains carbon monoxide, carbon dioxide, hydrogen chloride, chlorine, and sulfur compounds, such as H_2S, COS, etc. This gas stream is burned in a CO boiler and then caustic scrubbed to remove SO_x. The cost of SO_x control is shown in Volume VIII, page 46. If 80% of the SO_x is removed, the estimated emissions will be 10 lb SO_x/ton of alumina.

The electricity consumption in this alternative is 333 kWh/ton of alumina. Estimated emissions from the power boiler are 19 lb SO_x/ton of alumina, based on no control, and 4.2 lb SO_x/ton of alumina, based on control to meet the NSPS. Combining all sources, the total controlled SO_x emissions are 14.2 lb/ton.

Aluminum Production

Base Case Process - Hall-Heroult Process--

This process involves reduction of alumina to aluminum, using electrolytic cells. The existing plants use Soderberg electrodes and the new plants use prebaked electrodes which consume less energy. A detailed description of the process is given in Volume VIII, page 52.

Electrolytic cell operation produces particulate, sulfur, and hydrocarbon emissions, as well as fluoride emissions. The amount of emissions depend upon the type of cell used.

Prebake Cells and Soderberg Cells--

The electrolytic reduction of aluminum produces a CO exhaust at the anode of the cell. As the exhaust leaves the cell, it entrains particulates including fluoride salts. The exhaust also contains noxious gases such as HF and traces of H_2S.

In a prebake plant the carbon anode, which is consumed as a part of the reaction, is formed in a baking furnace. The manufacturing process is similar to coke-making in that a paste made of pitch and coal is devolatilized forming a solid carbon anode. This process emits large amounts of hydrocarbons, sulfur compounds, and particulates.

Plants which use Soderberg cells do not require anode furnaces because the anode is formed from a coke-based paste within the electrolytic cell itself. In this case, the particulate, sulfur and hydrocarbon emissions, common to the anode furnace of a prebake cell, will be emitted in the electrolytic cell of the Soderberg process instead.

SO_x Emissions--

Total SO_x emissions are estimated to be 60 lb/ton of aluminum, but of course dependent upon the sulfur content of the pitch and coke used to manufacture the anodes (Volume VIII, page 134) and cell type. Based on 85% control efficiency using scrubbers, controlled emissions are estimated to be 9 lb SO_x/ton of aluminum.

When current aluminum technology is used, major SO_x emissions are from the power boiler used to generate electricity and are estimated at 900 lb SO_x/ton of aluminum, with no control, and 200 lb SO_x/ton of aluminum, based on control at the power plant to meet the NSPS. The newer plants consume less electrical energy (12,000 kWh/ton of aluminum for the newer plants versus 15,600 kWh/ton of aluminum for older plants) and therefore the emissions from the power boiler are reduced to an estimated value of 700 lb SO_x/ton of aluminum based on no control and 150 lb SO_x/ton of aluminum based on control to meet the NSPS.

Process Option 1 - Alcoa Chloride Process--

This process starts with pot feed alumina from the Bayer process. The alumina is converted into aluminum chloride by chlorination in the presence of carbon to form volatile aluminum chloride. This, in turn, is purified and fed to the electrolytic cells to produce molten aluminum. Calculations below are Arthur D. Little estimates based on limited published data.

Energy consumed by the process includes No. 6 fuel oil equivalent to 24.8 x 10^6 Btu/ton of aluminum (Volume VIII, page 69). The estimated emissions are 41 lb SO_x/ton of aluminum based on 1% sulfur in the oil burned. The burned off gases from the coker must be treated to remove sulfur emissions. Because of the extremely high sulfur loadings expected, the stack scrubbing process used should be regenerative. Most of the scrubbing processes appropriate for this type of control were developed for utility boilers. Such systems include a scrubbing system (for gas-liquid contact) and an alkali handling system (for regeneration of caustic, for example). These systems have been proven effective on pilot-scale systems, and several full-scale systems are now in operation.

The SO_x control costs are shown in Volume VIII, page 67. The estimated controlled emissions are 8 lb SO_x/ton of aluminum based on 80% efficiency.

Based on the electricity consumption of 10,500 kWh/ton of aluminum (Volume VIII, page 69), emissions from the power boiler are estimated at 610 lb SO_x/ton of aluminum, based on no control, and 130 lb SO_x, based on control to meet the NSPS. The combined controlled emissions are then 138 lb SO_x/ton of aluminum, a slight improvement, achieved by reduced electricity consumption.

Process Option 2 - Refractory Hard Metal Cathodes Process--

This process is based on Bayer alumina and uses titanium diboride cathodes instead of conventional carbon cathodes. The cathodes are assumed to be retrofitted in existing large cells to increase production and reduce energy consumption (Volume VIII, page 74). A detailed process description is given in Volume VIII, page 68.

The emission loadings and control methods in this alternative are the same as in the base case process.

The electricity consumed in the process is 12,480 kWh/ton of aluminum (Volume VIII, page 76). Estimated emissions from the power boiler are 720 lb SO_x/ton of aluminum, based on no control, and 160 lb SO_x/ton of aluminum based on control to meet the NSPS. Total SO_x emissions are thus reduced by about 20%.

Process Option 3 - Combination of the Clay Chlorination Process and the Alcoa Chloride--

The details of the combined process are given in Volume VIII,

page 79. Since intermediate alumina production is eliminated, there is some reduction in emissions. The estimated emissions from the Toth process include 49 lb SO_x/ton of alumina. For aluminum production, 1.93 tons of alumina/ton of aluminum are required (Volume VIII, pages 50 and 81). Therefore, emissions are estimated to be 95 lb SO_x/ton of aluminum. The controlled emissions are estimated at 19 lb SO_x/ton of aluminum.

The electricity consumed in the process is 10,637 kWh/ton of aluminum (Volume VIII, page 81), resulting in an estimated emissions of 620 lb SO_x/ton of aluminum, based on no control, and 130 lb of SO_x/ton of aluminum based on control to meet the NSPS. The total controlled emissions would then be approximately 149 lb SO_x/ton, which is not significantly different from other anticipated technology.

Summary

The estimated SO_x emission factors for the alumina and aluminum industry are summarized in Table 13.

The major difference in the SO_x emissions in alumina production results from the use of coal in the nitric acid ion exchange and Toth processes. Natural gas is assumed to be used as fuel in the remaining alumina processes. Control methods include removal of SO_x in the bag filters (because of the alkaline nature of the particulate cake) and in wet scrubbers.

In the aluminum industry, the majority of the emissions come from the power boiler because of the consumption of large quantities of electricity. These emissions which are proportional to energy demand may be controlled by flue gas desulfurization and coal cleaning methods.

The SO_x emissions in the alumina and aluminum industry are summarized in Table 14. The process alternatives in aluminum production are aimed at reducing the consumption of electricity and therefore do reduce power boiler emissions concurrently.

SO_x emissions from the aluminum production are significantly higher (about 40 times) than those from the alumina production (Table 14). While a significant portion of aluminum manufacturing now relies on hydroelectric power, we expect that much of the incremental aluminum capacity to be installed in the next 15 years will be based on fossil fuels and, to a lesser extent, on nuclear power. Thus we believe the SO_x emissions calculated here are not unrealistic if the alumina/aluminum processes discussed are actually implemented and U.S. capacity growth projections are realized.

TABLE 13. ESTIMATED CONTROLLED SO_x EMISSION FACTORS - ALUMINA AND ALUMINUM INDUSTRY

Process	Emission factor - no control (lb/ton product)			Emission factor - with control (lb/ton product)			Control efficiency (%)
	Process	Power boiler	Total	Process	Power boiler	Total	
Alumina							
Base case: Bayer	0	16	16	0	3.3	3.3	79
• Hydrochloric acid ion exchange	0	8	8	0	1.7	1.7	79
• Nitric acid ion exchange	120	8	128	60	1.7	61.7	52
• Clay chlorination (Toth)	49	19	68	10	4.2	14.2	79
Aluminum							
Base case: Hall-Heroult (current practice)	60	900	960	~9	200	209	78
• Hall-Heroult (new)	60	700	760	~9	150	159	79
• Alcoa chloride	41	610	651	8	130	138	79
• Refractory hard metal cathode	60	720	780	9	160	169	78
• Combination of clay chlorination (Toth) and Aloca chloride	95	620	715	19	130	149	79

TABLE 14. ESTIMATED CONTROLLED SO_x EMISSIONS - ALUMINA AND ALUMINUM INDUSTRY

Process	Controlled SO_x emission factor (lb/ton product)				SO_x emissions (10^6 lb/yr)	
	Process	Power boiler	Total	Change in emission factor	1974	1989-1974*
Product: Alumina						
Base case:						
Bayer	0	3.3	3.3	--	25.4**	35.5
• Hydrochloric acid ion exchange	0	1.7	1.7	-1.6	--	18.3
• Nitric acid ion exchange	60	1.7	61.7	+58.4	--	663
• Clay chlorination (Toth alumina)	10	4.2	14.2	+10.9	--	153
Product: Aluminum						
Base case:						
Hall-Heroult (current practice)	9	200	209	--	1,045	1,463
• Hall-Heroult (new)	9	150	159	-50	--	1,113
• Alcoa chloride	8	130	138	-71	--	966
• Refractory hard metal cathode	9	160	169	-40	--	1,183
Base case:						
Bayer and Hall-Heroult (c.p.)	9	206***	215	--	1,070**	1,505
• Toth alumina and Alcoa chloride	19	130	149	-66	--	1,043

(continued)

TABLE 14.(continued)

*Based on multiplying emission factor by increments in production from 1974 to 1989 of 10.75 million tons alumina/year and 7.0 million aluminum tons. This assumes no retirement of 1974 facilities.

**Estimated 1974 emissions, based on the emission factor of 3.3 lb SO_x/ton of alumina, are $3.3 \times 7.7 \times 10^6 = 25.4 \times 10^6$ lb SO_x from alumina production; and, based on the emission factor of 209 lb SO_x/ton of aluminum, are $209 \times 5 \times 10^6 = 1{,}045 \times 10^6$ lb SO_x from aluminum production; resulting in a total of $1{,}070 \times 10^6$ lb SO_x from alumina and aluminum.

***Bayer process, plus Hall-Heroult process (current practice), is used for comparative analysis based on 1.93 tons alumina per ton aluminum (Volume VIII, P. 116).
C.P. - current (1974) practice

PULP AND PAPER

Chemical Pulp

Base Case Process - Kraft Pulping--

The base case process selected for chemical pulp was the Kraft process, which includes cooking of wood chips at elevated temperature and pressure in a digester. When cooking is completed, the contents of the digester are forced into the blow tank where the spent cooking liquor is drained. After unreacted chunks of wood are removed, the pulp is washed, bleached, pressed, and dried into the finished product. Further details are found in Volume 5, page 55.

Recovery of both the inorganic cooking chemicals and the heat content of the spent liquor, which is separated from the cooked pulp in the blow tank, is economical. Recovery is accomplished by first concentrating (in an evaporator) the liquor to a level that will support combustion and then feeding it to a furnace (recovery boiler) where heat recovery takes place. This is followed by chemical recovery in a smelt dissolving tank.

The characteristic odor of the Kraft mill is partially caused by hydrogen sulfide. The major source is the direct contact evaporator in which the sodium sulfide in the black liquor reacts with the carbon dioxide in the furnace exhaust. In addition, the Kraft-process odor also results from an assortment of organic sulfur compounds, all of which have extremely low odor thresholds. These compounds are emitted from many points within a mill; however, the main sources are the digester/blow tank systems and the direct contact evaporator.

The lime kiln can also be a potential source as a similar reaction occurs involving residual sodium sulfide in the lime mud. Lesser amounts of hydrogen sulfide are emitted with the non-condensible off-gases from the digesters and multiple-effect evaporators.

Sulfur dioxide emissions result mainly from oxidation of reduced sulfur compounds in the recovery furnace. Sulfur dioxide may also be present in the power boiler effluent gas, depending on the sulfur content of the fuel used.

The uncontrolled total reduced sulfur (TRS) emissions from the Kraft process are shown in Table 15. The emissions are expressed as equivalent weights of sulfur. The EPA is planning to establish air pollution emission standards for new Kraft pulp mills with proposed standards shown in Table 15. The control method for eliminating reduced sulfur compounds (TRS) is oxidation to SO_x. The uncontrolled TRS emissions from the various process steps are 24^{x} lb TRS/ton of pulp (Table 15) and will result in emissions of 48 lb of SO_x (as SO_2) per ton of pulp.

TABLE 15 UNCONTROLLED EMISSIONS OF TRS AND PROPOSED EMISSION STANDARDS FOR NEW KRAFT PULP MILLS

	Uncontrolled emissions of TRS (lb/ton of pulp*)	Proposed standard for TRS (ppm)	(lb/ton of pulp)*
Recovery boiler	15	5**	0.15
Lime kiln	Trace	5***	0.025
Smelt tank	0.1	5***,****	0.025****
Brown stock washer*****	1.0	5	0.01
Black liquor oxidation*****	N.A.	5	0.01
Condensate stripping******	N.A.	5	0.01
Digester******	8	5	0.01
Multiple effect evaporator******	N.A.	5	0.01
Bleaching	Negligible	5	0.01
Lime slaker	Trace		
TOTAL	∿ 24		

* Air-dried basis.

** TRS corrected to 8% oxygen.

*** TRS corrected to 10% oxygen.

**** Fresh water will ensure compliance.

***** Likely control method is utilization of gas stream as combustion air in the recovery furnace.

****** Likely control method is utilization of gas stream as combustion air in the lime kiln.

Combination boilers (bark and oil, or bark and coal) or bark boilers are used as on-site power boilers in the pulp and paper industry. The discharge from a bark boiler consists of gaseous products of combustion containing negligible sulfur compounds. The combination boiler (coal and bark) will have SO_x emissions in proportion to the consumption of coal and the sulfur content of the coal. The estimated emissions based on the consumption of 1.4×10^6 Btu fossil fuel (containing 3.5% sulfur in coal) per ton of pulp are 7.8 lb SO_x/ton of pulp from the boiler. If these emissions are controlled, the estimated controlled emissions will be 1.7 lb SO_x/ton of pulp.

The energy credits in the Kraft process include 140 kWh/ton of pulp (Volume V, page 57). Thus, the estimated reduction in emissions at the power boiler are 8.1 lb SO_x/ton of pulp, with no control, and 1.8 lb SO_x/ton of pulp, based on SO_x controlled to meet the NSPS. Therefore, the net estimated reduction in emissions from the above two power boilers is 0.3 lb SO_x/ton of pulp, with no control, and 0.1 lb/ton of pulp, based on control to meet the NSPS. Total SO_x controlled emissions are estimated at 47.9 lb/ton.

Process Option 1 - Alkaline-Oxygen Pulping--

The alkaline-oxygen (A-O) pulping process is receiving industry interest because of its potential for a non-sulfur cooking step, which would eliminate the air pollution due to sulfur compounds. The steps in the A-O process include an alkaline treatment to soften the wood chips, mechanical disintegration, and treatment with oxygen under alkaline conditions to remove most of the lignin. This is followed by the last three stages of the conventional multistage bleaching sequence: chlorine dioxide, caustic extraction, and(chlorine dioxide). A detailed description of the process is given in Volume V, page 84.

Because sulfur is not used in the process, chemicals containing sulfur are not present in the air emissions. However, SO_x may be present in the air emissions from the lime kiln and the power boiler because of the sulfur present in the fuel. The emission factor for fuel combustion in lime kilns is not available. It is expected that a major fraction of the SO_x will be absorbed by the alkali dust in the kiln and by the air pollution control device, provided wet scrubbers or bag filters are used. The estimated emissions from the on-site power boiler are 18.3 lb SO_x/ton of pulp and the estimated controlled emissions are 4.0 lb SO_x/ton of pulp. The emissions are based on consumption of coal containing 3.5% sulfur at a rate equivalent to 3.3×10^6 Btu/ton of pulp. The energy credits in the A-O process include 50 kWh/ton of pulp (Volume V, page 90). Thus, the estimated reduction in emissions at the power boiler is 2.9 lb SO_x/ton of pulp and the estimated reduction in the controlled emissions is 0.63 lb SO_x/ton of pulp.

The net total emissions from the A-O process are 15.4 lb SO_x/ton of pulp, with no control, and the net total controlled emissions are 3.37 lb SO_x/ton of pulp -- a very significant improvement over the conventional Kraft process.

Process Option 2 - Rapson Effluent-Free Kraft Process--

A number of changes in the base case Kraft process have been made to eliminate effluents in the Rapson process. These changes are described in detail in Volume V, page 95, and include closing the water cycle, use of chlorine dioxide rather than Cl_2, countercurrent washing, etc.

The air emissions from the process are not affected by the above changes and the emissions are 24 lb TRS/ton of pulp (Volume V, page 104). The emissions from the on-site power boiler are less because of reduced consumption of purchased fuel (coal). The total energy consumed in the process, excluding that required for the lime burning, is 0.7×10^6 Btu/ton of pulp (Volume V, page 101). The estimated emissions are 3.88 lb SO_x/ton of pulp with no control, and the estimated controlled emissions are 0.84 lb SO_x/ton of pulp. Electricity from the on-site power boiler is sufficient for the process requirements in this alternative.

Newsprint Pulp

Base Case Process - Refiner Mechanical Pulping (RMP) Process--

RMP is a mechanical pulping process that is an improvement over the conventional groundwood process. Wood chips, sawdust, and shavings from sawmills or plywood mills can be used as raw materials for the RMP process, but such materials cannot be used as raw materials for the groundwood process. The wood particles are reduced to fibers in a pressurized disc refiner which consists of two circular metal plates that generally rotate in opposite directions. The RMP pulp (80%), together with Kraft pulp (20%), is used in newsprint paper production. A detailed description of the RMP process is given in Volume V, page 60.

There are no emissions containing sulfur compounds from the RMP process, except those from the power boiler. The purchased electricity is 1,475 kWh/ton of pulp. Therefore, the estimated emissions from the power boiler are 85.6 lb SO_x/ton of pulp, with no control, and the estimated controlled emissions are 18.6 lb SO_x/ton of pulp. Of course, if hydroelectric power is used, no SO_x emissions would occur.

The newsprint pulp consists of 80% RMP pulp and 20% Kraft pulp (Volume V, page 112). Therefore, the estimated uncontrolled emissions are 4.8 lb TRS/ton of newsprint pulp from the process and 68.4 lb SO_x/ton of newsprint pulp from the on-site and utility power boilers. The estimated controlled emissions are 9.6 lb SO_x/ton of newsprint pulp (TRS converted to SO_x) from the process and 14.9 lb SO_x/ton of newsprint pulp from the power boilers for a total of 24.5 lb SO_x/ton.

Process Option 1 - Thermo-Mechanical Pulping (TMP)--

The TMP process is similar to the base case process (RMP process), except that the wood particles are preheated to 130°C for a short period

and then reduced to fibers in a pressurized disc refiner. A detailed process description is given in Volume V, page 104.

The emissions from the TMP process are identical to those from the base case process, except that the newsprint pulp can be composed of 95% TMP pulp and 5% Kraft pulp. Therefore, the estimated uncontrolled emissions are 1.2 lb TRS/ton of newsprint pulp from the process and 81.3 lb SO_x/ton of newsprint pulp from the on-site and utility power boilers. The estimated controlled emissions are 2.4 lb SO_x/ton of newsprint pulp from the process (TRS converted to SO_x) and 17.7 lb SO_x/ton of newsprint pulp from the power boilers, totaling 20.1 lb/ton, an 18% reduction per ton of newsprint pulp.

Process Option 2 - De-inking of Old News for Newsprint Manufacture--

The de-inking of old news for newsprint manufacture is a well-established commercial practice and a detailed description of the process is given in Volume V, page 113. The only emissions from the process are those generated in the power boilers (on-site and utility). The total energy required is 6.1×10^6 Btu/ton of newsprint pulp. Therefore, the estimated emissions are 33.8 lb SO_x/ton of newsprint pulp, with no control, and 7.32 lb SO_x/ton of newsprint pulp based on control to meet the NSPS.

Summary

The emission factors and total emissions for the base case processes and alternative processes are summarized in Tables 16 and 17. The emissions in the alkaline-oxygen pulping alternative are significantly lowered due to elimination of compounds containing sulfur from the process. The emissions from pulp and paper mills generally are not controlled, except that the form of sulfur in the emissions is changed from reduced sulfur to sulfur oxides. Newsprint based on TMP and RMP processes results in smaller emissions than the base case process, largely because of the smaller fraction of Kraft pulp. De-inking benefits from an absence of sulfur-containing compounds in the de-inking of old news for newsprint manufacture.

On a national scale A-O pulping would have the greatest impact in reducing SO_x emissions.

GLASS

Base Case Process - Regenerative Furnace

The base case process selected was the natural gas-fired furnace with cold charge. A detailed description of the furnace is given in Volume XI, page 17. Operating conditions for the base case process are:

TABLE 16. ESTIMATED SO_x EMISSION FACTORS - PULP AND PAPER INDUSTRY

Process	Emission factor* - no control (lb/ton of pulp)**			Emission factor* - with control (lb/ton of pulp)**			Control Efficiency (%)
	Process	Boiler	Total	Process	Boiler	Total	
Base case:							
Kraft pulping	48	-0.3	47.7	48	-0.1	47.9	--
• Alkaline-oxygen pulping	0	15.4	15.4	0	3.37	3.4	-78
• Rapson effluent-free Kraft pulping	48	3.88	51.9	48	0.84	48.8	-6
Base case:							
Newsprint - RMP	9.6	68.4	78.0	9.6	14.9	24.5	-69
• Newsprint - TMP	2.4	81.3	83.7	2.4	17.7	20.1	-76
• De-inking of old news for newsprint manufacture	0	33.8	33.8	0	7.3	7.3	-78

*Reported as lb SO_2/ton of ADP. The uncontrolled process emissions are present as TRS compounds.

**Air-dried basis.

TABLE 17 -- ESTIMATED CONTROLLED SO_x EMISSIONS: PULP AND PAPER INDUSTRY

Process	Emission factor (lb/ton of pulp)* Process	Boiler	Total	Change in emission factor	SO_x emissions (10^6 lb/yr) 1974	1989-1974**
Base case: Kraft pulping	48	-0.1	47.9	--	766***	829
• Alkaline-Oxygen(A-O) pulping	--	3.37	3.4	-44.5	--	58.8
• Rapson effluent-free Kraft pulping	48	0.84	48.8	+0.9	--	844
Base case: Newsprint - RMP	9.6	14.9	24.5	--	95.6***	42
• Newsprint - TMP	2.4	17.7	20.1	-4.4	--	34
• De-inking of old news for newsprint manufacture	--	7.3	7.3	-17.2	--	12

*Air-dried basis.

**Based on increment in production from 1974 to 1989: 17.3×10^6 tons of Kraft pulp and 1.7×10^6 tons of newsprint pulp.

***Estimated 1974 emissions, based on the total emission factor of 47.9 lb/ton of Kraft pulp are $47.9 \times 16 \times 10^6 = 766 \times 10^6$ lb SO_x /yr from the Kraft pulp process and, based on the total emission factor of 24.5 lb/ton of newsprint pulp, are $24.5 \times 3.9 \times 10^6 = 95.6 \times 10^6$ lb SO_x/yr from the newsprint pulp process.

Furnace type: - Side port, regenerative
Fuel: - Natural gas
Glass type: - Soda lime
Plant location: - East North Central
Pull rate: - 200 tons per day
Feed rate: - 240 tons per day
Efficiency: - 90%, or 180 tons per day.

The typical glass melting operation is described in detail in Volume XI, page 19. A glass-melting furnace has both particulate and gaseous emissions which must be controlled.

The sulfur oxide emissions arise from two sources: sulfur in the fuel and decomposition of mineral sulfates in the glass melt. The sulfur within the fuel (natural gas) is generally a minor source of sulfur oxide emissions and generally results in the production of SO_2. The decomposition of mineral sulfates in the melt produces SO_3. Although some SO_3 decomposes to SO_2 at temperatures above 2790°F, some will remain in the form of SO_3. The emission factor for the glass furnace is 3.0 lb SO_x/ton of glass (Volume XI, page 27).

The emissions containing high concentration of SO_3 are expected to increase the corrosion potential and make air pollution control more difficult. The control techniques for SO_2 and SO_3 consist of contacting the gases with caustic or lime to convert the gaseous emissions to sulfate or sulfite salts of sodium or calcium. Scrubbers for this purpose should utilize high-efficiency entrainment separators to avoid carryover of sulfuric acid mist.

Other add-on control systems include Dry Tesisorb systems*. The Tesisorb X (chemical composition not available), which is added upstream of the bag filter, is capable of collecting gaseous pollutants. The reaction products are solid inorganic particles and are removed in the bag filter. The bag filter is operated at 200°F. The outlet SO_x concentration is less than 50 ppm, equivalent to 0.7 lb SO_x/ton of glass.

The estimated emissions from the power boiler to generate electricity are 1.1 lb SO_x/ton of glass with no control, and 0.24 lb SO_x/ton of glass based on control to meet the NSPS.

Process Option 1 - Coal Gasification

Coal gasification processes include, with some variation, the following steps: coal handling and storage, coal preparation, gasification, oxidant feed facilities, and gas cleaning. The gas produced from coal gasification is used as a fuel source in the glass furnace. The

*Marketed by Teller Environmental Systems, Worcester, Mass.

details of the process are given in Volume XI, page 32.

When coal gasification is used to generate the gaseous fuel for the glass melting furnace, the major environmental difference is not in the glass-making process, but rather in the fuel-generating process.

The fuel gas produced in the coal gasifier will contain sulfur, mainly in the form of H_2S. So that excessive SO_2 emissions do not occur, the sulfur must be controlled either before or after gas combustion in the furnace. Two control technologies could be considered: a sulfur-recovery process, such as the Stretford process, to remove H_2S from the fuel gas prior to burning the fuel in the furnace, or flue gas desulfurization, such as the processes currently used on utility boilers for removing SO_2 from exhaust gases. The latter case is the same as the control for direct coal firing (as discussed below).

The estimated emissions from burning of coal are 47.0 lb SO_x/ton of glass based on no control. Thus, the total uncontrolled emissions are 50.0 lb SO_x/ton of glass (includes 3.0 lb SO_x/ton of glass from mineral sources). If the Stretford process (sulfur collection efficiency of 90%) is used to collect sulfur compounds, the estimated emissions from the glass furnace are 7.7 lb SO_x/ton of glass. The estimated capital and operating costs for the Stretford process are given in Volume XI, page 39.

The SO_x can be further removed in the wet scrubber or Tesisorb systems. The estimated concentration of SO_x in the tail gas will be 50 ppm, equivalent to 0.77 lb SO_x/ton of glass. The emission factor is based on an estimated 10% higher gas flow rate compared to that in the base case process.

The SO_x emissions from the power boiler are comparable to those from the base case process, and are about 1.1 lb SO_x/ton of glass with no control, and about 0.24 lb SO_x/ton of glass based on control to meet the NSPS. Therefore, the total SO_x emissions after control are only slightly increased to 1.01 lb/ton.

Process Option 2 - Direct-Coal-Firing

In this option, pulverized coal is used directly in burners to supply the energy. The details of the process are in Volume XI, page 35.

Coal is high-sulfur fuel (3.5% sulfur), so SO_x will be present in the flue gas. The uncontrolled emissions in this alternative will be comparable to those from a coal gasification process, and amount to 50 lb SO_x/ton of glass.

The emissions may be controlled in a wet scrubber. Calcium or

sodium-based alkali may be used in the scrubber. The cost of alkali will be significantly higher because of high concentrations of SO_x. The SO_x concentration in the outlet gas may be reduced to about 200 ppm. The gas flow rate in this alternative is about 10% higher than that from the base case process. Therefore, the estimated controlled emissions are 3.1 lb SO_x/ton of glass.

The SO_x emissions from the power boiler in this alternative are comparable to those from the power boiler in the base case process, about 1.1 lb SO_x/ton of glass with no control, and 0.24 lb SO_x/ton of glass based on control to meet the NSPS. The total then is a significantly higher 3.3 lb/ton.

Process Option 3 - Coal-Fired Hot Gas Generation (COHOGG)

This system generates a hot gas by separating char and volatiles, burning the char, and then mixing the products of combustion with the volatiles and burning them together. A pneumatic conveying system feeds powdered coal to the pyrolyzer along with limestone or a mix of limestone and sodium chloride. The outlet temperature of the gases leaving the afterburner is 3,000°F. These hot gases are used in the glass melting furnace to heat the glass batch. The details of the process are given in Volume XI, page 48.

From one-third to one-half of the sulfur in the coal is expected to come off in the pyrolyzer as hydrogen sulfide (H_2S). The limestone, in turn, reacts with the hydrogen sulfide, producing water and calcium sulfide (CaS). Unreacted limestone, char, and calcium sulfide go to the char burner, which is a fluidized-bed combustor, where the remaining sulfur forms SO_2. There the remaining limestone from the pyrolyzer step reacts with the SO_2, forming calcium sulfite* which leaves the bed along with the ash from the char.

The only difference between the coal gasification alternative and that of heating the glass-melting furnace with a hot combustion gas is that the sulfur control in the latter option is inherent within the process itself and is not required as a part of the pollution control apparatus. The gas volumes to the glass furnace are higher with the COHOGG process because of the efficiency losses inherent in the system. Except for the slight size difference, however, the pollution control system for the glass melting furnace itself will be the same as for coal gasification. The concentration of SO_x in the tail gas is about the same as that in the coal gasification process with SO_x control (Stretford process). However, because of the higher gas flow rates (25% higher compared to the gas flow rate from the coal gasification process; see Volume XI, page 40 for details), the emission factor with control will be about 1.0 lb SO_x/ton of glass for COHOGG.

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*Some sulfates are also formed.

The SO_x emissions from the power boiler in this alternative are comparable to those from the base case process, or about 1.1 lb SO_x/ton of glass with no control, and about 0.24 lb SO_x/ton of glass based on control to meet the NSPS. Total controlled emissions, at 1.24 lb/ton, are 32% larger than the base case.

Process Option 4 - All-Electric Melting Process

Molten glass can be heated by the passage of an electric current. Both the design and the operation of an all-electric, glass-melting furnace differ greatly from those of the typical natural gas-fired, regenerative furnace. The electric furnace without its regenerative checker structure is a much simpler design. The details of the electric furnace are given in Volume XI, page 53.

The option to heat glass-melting furnaces electrically results in a shift in the environmental problems from the furnace to the electric power generating plant. In this case, the only exhaust from the glass-melting furnace is from the decomposition of carbonates, sulfates, nitrates, etc., in the glass batch. The exhaust will be almost entirely CO_2 with approximately 3 lb SO_x/ton of glass (Volume XI, page 27).

The control system for this exhaust is identical to the one used for the base case and for coal gasification, but the size of the system is considerably smaller because of the greatly reduced exhaust volume. If the SO_x emissions are assumed to be controlled to 200 ppm, the emissions will be reduced to 0.1 lb SO_x/ton of glass.

The electricity consumption is increased in this alternative to 780 kWh/ton of glass. Therefore, the estimated emissions from the power boiler are 45.2 lb SO_x/ton of glass, with no control, and 9.82 lb SO_x/ton of glass, based on control, to meet the NSPS. Total controlled emissions are significantly increased, at 9.82 lb/ton.

Process Option 5 - Batch Agglomeration/Preheating

The intent of preheating is to prereact the batch ingredients. Batch preheating is an energy-conserving technology relating to a furnace modification rather than a method of furnace heating. Hence, this technology is applicable to all of the previously discussed methods of heating, except for electric heating. The details of the process are given in Volume XI, page 58.

The uncontrolled SO_x emissions from this process alternative are comparable to those from the base case process, or about 3.0 lb SO_x/ton of glass. The gas flow rate is about 20% lower than that from the base case process.

The control methods used in the base case process may be used here. If the SO_x emissions are controlled to a concentration of 50 ppm, the

estimated emission rate is 0.56 lb SO_x/ton of glass.

The SO_x emissions from the power boiler in this alternative are comparable to those from the base case process, or about 1.1 lb SO_x/ton of glass, with no control, and 0.24 lb SO_x/ton of glass, based on control to meet the NSPS. Thus applying preheating, even to the conventional furnace, can reduce SO_x emissions by about 15%.

Summary

The emission factors and total emissions for the flat glass industry are summarized in Tables 18 and 19.

The uncontrolled emissions from the base case process and process alternative depend on the sulfur content of the fuel. Processes based on natural gas obsiously have significantly lower emissions compared to those from the processes based on coal, as expected.

The controlled emissions depend on the extent of control. The controlled emissions range from 0.8 to 10 lb SO_x/ton of glass. Also, the SO_x emissions from the electric melting process alternative are the highest because of emissions from the electric power generating site. Preheating appears to be an attractive alternative because both energy is saved and SO_x emissions are reduced.

COPPER

Base Case Process - Conventional Copper Smelting

Conventional smelting involves the smelting of sulfide concentrates in the reverberatory furnace either directly or after roasting. The mixture of molten sulfides from the reverb is converted to blister copper in converters. A detailed description of this process is given in Volume XIV, page 23. The capacity of the base case smelter is 100,000 tons of anode copper per year.

With over 30% sulfur, most copper concentrates contain more sulfur than copper. About 1-2% of the sulfur entering the smelter is lost in the slag and perhaps 3-4% evolves as fugitive emissions. The remaining sulfur is lost/discharged in gaseous emissions from roaster, reverb, and converters. Typical sulfur distributions from conventional smelting are:

Source	Calcine Smelting (%)	Green Charge Smelting (%)
Roaster	20	--
Reverb	25	40
Converter	50	55
Slag and Fugitives	5	5
Total	100	100

TABLE 18. ESTIMATED SO_x EMISSION FACTORS - GLASS INDUSTRY

Process	Emission factor* - no control (lb/ton of glass)			Emission factor* - with control (lb/ton of glass)			Control Efficiency
	Process	Power boiler	Total	Process	Power boiler	Total	%
Base case: Regenerative furnace	3	1.1	4.1	0.7	0.24	0.94	77
• Coal gasification	50	1.1	51.1	0.77	0.24	1.01	92
• Direct coal firing	50	1.1	51.1	3.1	0.24	3.34	93
• Coal fired hot gas generation	50	1.1	51.1	1.0	0.24	1.24	98
• Electric melting	3	45.2	48.2	0.1	9.82	9.92	79
• Batch preheat with natural gas firing	3	1.1	4.1	0.56	0.24	0.80	80

*Reported as lb SO_2/ton of glass.

TABLE 19. ESTIMATED CONTROLLED SO_x EMISSIONS - GLASS INDUSTRY

Process	SO_x emission factor for glass production (lb/ton of glass)			Change in Emission factor	SO_x emissions (10^6 lb/yr)	
	Process	Boiler	Total		1974	1989-1974*
Base case:						
Regenerative furnace**	0.7	0.24	0.94	--	27.3**	12.2
• Coal gasification	0.77	0.24	1.01	+0.07	--	13.1
• Direct coal firing	3.1	0.24	3.34	+2.40	--	43.4
• Coal-fired hot gas generation	1.0	0.24	1.24	+0.30	--	16.1
• Electric melting	0.1	9.82	9.92	+8.98	--	129
• Batch preheat with natural gas firing	0.56	0.24	0.80	-0.14	--	10.4

*Based on increment in production from 1974-1989 = 13 x 10^6 ton/yr. (see Table 1)

**Estimated 1974 emissions, based on the total emission factor of 0.94 lb SO_x/ton of glass, are 0.94 x 29 x 10^6 = 27.3 x 10^6 lb/yr.

The estimated total uncontrolled emissions based on the 28.6% copper and 33.4% sulfur in the copper sulfide concentrate are 2.31 tons of SO_2/ton of copper.

SO_x emissions from smelters are controlled by the New Source Performance Standards (NSPS) as follows:

- Emissions from streams containing high concentrations of SO_2 (converter and roaster gases) have to be controlled by technology such as sulfuric acid plants. Double absorption plants (or equivalent) are mandatory for new sources. This combination of uncontrolled reverbs but controlled roasters and converters can recover about 50-70% of the sulfur in the feed in the form of sulfuric acid.

- New Source Performance Standards would allow the use of reverbs only for the smelting of "impure" concentrates (concentrates containing As, Sb, Bi, etc.), but reverb emissions would not have to be treated for SO_2 removal. About 30% of the feed sulfur is emitted from the reverbs.

- Federal Ambient Air Quality Standards (AAQS's) which define permissible ground level concentrations of SO_2 have to be met at all times by a combination of permanent controls (e.g., acid plants) and production curtailment. The issue -- when should production curtailment be used -- has not been resolved. The degree of permanent controls necessary to meet Ambient Air Quality Standards varies greatly with location. The control of roaster or converter emissions is adequate for meeting Ambient Air Quality Standards only in certain locations.

At present, there are three control methods in use at copper smelters for reducing the sulfur dioxide concentrations in the vicinity of a smelter: (1) the use of a tall stack to disperse dilute gas streams; (2) the production of sulfuric acid by the contact process from concentrated gas streams to achieve a degree of reduction in emissions; and (3) production curtailment.

The contact sulfuric acid process is well established for treating SO_2-containing off-gases from metallurgical plants. Modern contact acid plants require at least 4.5-5% sulfur dioxide in the feed gas to operate autogenously (i.e., without external heat). For handling lower concentrations of SO_2, an additional fuel input is required. Acid plant size is primarily a function of the volume of gas handled. Thus, for a constant acid output, an acid plant operating on more dilute gases is much larger (and more expensive) than an acid plant operating on more concentrated gases. With the currently used vanadium pentoxide catalysts, the upper level of SO_2 concentration in the feed gas to an acid plant is between 7% and 9%. More concentrated gas streams require dilution.

Conventional smelters are located in geographical areas where acid markets are unavailable and where all SO_2-containing gas streams are vented to the atmosphere (after particulate control, if necessary). Streams from the roaster and converter, handled to minimize air leakage, contain SO_2 concentrations greater than 4-5%, which is adequate for autogenous sulfuric acid manufacture--the most cost-effective control technology for removing SO_2 from such streams. The reverb gases are a high-volume (up to 100,000 scfm) and low-concentration (0.5-2% SO_2) stream, not amenable to autogenous sulfuric acid manufacture and have to be discharged via tall stacks. In short, the emission sources of SO_x from a controlled conventional smelter are:

- Reverb gas - 82,000 scfm with 0.5-2% SO_2
- Acid plant tail gas - 38,800 scfm with 0.2% SO_2
- Anode furnace gas - data not available, contains some SO_2.

The above controlled emissions are equivalent to about 1,400 lb SO_x/ton of copper, representing a 70% control efficiency.

The electricity consumed in the copper smelting varies from 347 to 441 kWh/ton of copper. The estimated uncontrolled emissions at the power boiler are 20.0-25.6 lb SO_x/ton of copper and the estimated controlled emissions are 4.4-5.6 lb SO_x/ton of copper.

Process Option 1 - Outokumpu Flash Smelting

The flash smelting alternative combines the separate roasting and smelting operations of conventional copper extraction into one combined roasting/smelting process. The major advantages of the method are a reduction in fuel used for smelting and production of a gas stream having a concentration of SO_2 which is suitable for sulfuric acid manufacture. A detailed description of the process is given in Volume XIV, page 41.

The concentration of SO_2 in flash smelter gas is high, containing up to 13% SO_2. Conventional reverberatory furnace gas, on the other hand, typically contains 0.5-2.0% SO_2. The high-strength gases are most suitable for the manufacture of sulfuric acid. The variable strength/variable volume SO_2 gas stream from converters can be mixed with the steady stream of flash smelter gas to provide a stream high enough in SO_2 for acid manufacture. At high matte grades, a large amount of sulfur is eliminated in the flash furnace. This improves acid plant performance, because the volume and strength of the input stream are more constant.

The emissions from the acid plant tail gas represent the major source of pollutants from the Outokumpu smelter (55,000 scfm, 0.05% SO_2). The sulfur loss in various process streams includes 0.07% in drying,

1% each in smelting and converting, 0.1% in the anode furnace, and 1.2% in slag. The total sulfur emissions to the atmosphere are 2.8% of the sulfur in the feed (Volume XIV, page 216).

The estimated uncontrolled emissions from the copper smelter are 4,620 lb SO_2/ton of copper, and the controlled emissions are 133 lb SO_2/ton of copper.

The emissions from the power boiler are estimated at 21.1 lb SO_x/ton of copper with no control, and 4.6 lb SO_x/ton of copper based on control to meet the NSPS. The emissions are based on the electricity consumption of 366 kWh/ton of copper (Volume XIV, page 52). Obviously, the use of flash smelting, facilitating and recovery, allows the dual benefits of energy saving and SO_x reduction.

Process Option 2 - Noranda Process

The Noranda process combines the three operations of roasting, smelting, and converting of copper concentrates in a single reactor. The heat losses suffered during the transfer of concentrate from the roaster to the reverberatory furnace, are suppressed, as well as those occurring during the transfer of the matte from the reverberatory furnace to the converter. A detailed description of the process is given in Volume XIV, page 55.

The sulfur dioxide concentration in the reactor atmosphere is around 23% on a dry basis. Because of air infiltration around the hood, the gas stream entering the acid plant contains 10-13% SO_2. This stream is only interrupted 5% of the time during tapping, and can be mixed with the off-gases of other reactors and Pierce-Smith converters. Air in-leakage (thereby preventing atmospheric emissions) is high, but does not affect the subsequent H_2SO_4 plant, because its operation is at or below the 10-13% SO_2 concentration. This steady, high-SO_2, gas-generation level is a significant advantage over the conventional reverberatory process.

After dry-gas cleaning, wet-gas cleaning equipment is required to scrub out the remaining fine particulates. The gas can then be treated in a double-contact acid plant. Total sulfur recovery is as high as that achieved with the Outokumpu flash smelting process.

The SO_x emissions from the power boiler in this alternative are the same as in the Outokumpu flash smelter process, 21.1 lb SO_x/ton of copper, with no control, and 4.6 lb SO_x/ton of copper, based on control to meet the NSPS.

Process Option 3 - Mitsubishi Process Alternative

The Mitsubishi process consists of three metallurgical stages, each of which is carried out in a separate furnace. Thus, there is a smelting furnace for concentrates, a converting furnace to oxidize iron

in the matte and make blister copper, and a slag cleaning furnace. Intermediate products in the molten state move continuously among the respective furnaces, which are thus functionally connected with each other. A detailed description of the Mitsubishi process is given in Volume XIV, page 71.

On leaving any of the three furnaces, the mixed off-gases are expected to average over 10% SO_2 when the smelting furnace is operated with air enriched to 25% oxygen. This steady, high-SO_2 gas generation is a significant advantage over the conventional reverberatory process, as sulfur can be readily recovered as sulfuric acid. Since the molten liquids flow continuously over very short distances, minimum air pollution is generated in transfer operations, and "converter aisle losses" typical of conventional operations are avoided. Thus, fugitive emissions are expected to be lower than for conventional or for Outokumpu and Noranda (matte) processes.

After cooling and dry cleaning in electrostatic precipitators (or fabric filters operated above the dew point), the collected off-gases usually require a wet cleaning stage to remove any fine particulates and cool the gas to remove excess moisture. The cleaned gases are then admitted to a double-contact acid plant for H_2SO_4 manufacture. Total sulfur recovery is over 90%, as with all these advanced pyrometallurgical processes.

The acid plant tail gas flow rate and SO_x concentrations in the gas are comparable to those from the Outokumpu smelter. The emissions from the power boiler are the same as in the Outokumpu flash smelter process, or about 21.1 lb SO_x/ton of copper, with no control, and 4.6 lb SO_x/ton of copper based on control to meet the NSPS.

Process Option 4 - The Use of Oxygen in Smelting Process Alternative

Copper smelting can be conducted with pure oxygen or by using oxygen-enriched air. An increase in oxygen concentration will result in higher process temperatures. A detailed description is given in Volume XIV, page 82. The specific example selected for examination is Outokumpu flash smelting. Oxygen enrichment results in the reduction of effluent volume; however, the operating temperatures are generally increased.

Use of oxygen will result in reduced effluent volumes. The total uncontrolled SO_x emissions from the smelter will remain the same. If the emissions are controlled to a constant exit concentration, the controlled emissions will be reduced in direct proportion to the gas volume. The interplay between air preheat, oxygen enrichment, and fuel use is extremely complex and is described in more detail in Volume XIV, page 84. This report concluded that use of oxygen does not lead to any significant energy savings in the copper sector.

Process Option 5 - Metal Recovery from Slag Process Alternative

In conventional copper smelting, converter slag is recycled to the reverb and all the slag tapped from the revert is discarded. The copper contained in the discarded slag is lost. The amount of copper lost in the slag is significant, at about 1.5 to 3% or more of the copper in the feed materials. The processes for recovering metal from slag are described in Volume XIV, page 89. Since there is little sulfur in the slag, the process SO_x emissions are minor. The major source is the power boiler, but it is impossible to quantify these without a detailed analysis. In the copper sector these SO_x emissions would be relatively small.

Process Option 6 - The Arbiter Process Alternative

The Arbiter process is a hydrometallurgical process. A process description is given in Volume XIV, page 95. The Arbiter process causes little air pollution. The process is energy-intensive and uses large quantities of electricity and steam. As reported in Volume XIV, page 104, steam consumption is 20,000 lb/ton of copper, and electricity consumption is 3,000 kWh/ton of copper. The estimated emissions for the power plant are 284 lb SO_x/ton of copper with no control, and 62 lb SO_x/ton of copper based on control to meet the NSPS.

Summary

The emission factors and total emissions in the copper industry are summarized in Tables 20 and 21. The uncontrolled emissions from the pyrometallurgical processes are essentially the same. There are no SO_x emissions from the Arbiter process. The emissions from the power boiler in the Arbiter process are significantly higher than other processes. However, the total uncontrolled emissions from the Arbiter process are about 5% of those from other processes.

The emissions from the pyrometallurgical processes are controlled by add-on control technology, mainly acid plants. The control efficiency is only 70% in the conventional smelting process and over 90% in the other newer technologies proposed in the options, which also offer energy advantages. Therefore, on these two bases, it can be expected that the newer approaches will see rapid implementation as plants are replaced or additional capacity installed.

CHLOR-ALKALI

Some process changes have little direct affect on SO_x emissions and thus received little or no attention in the Industry Reports (Volumes I-XV). However, indirect SO_x emissions by differing electric energy or steam requirements between base case and alternative technology may arise. Generally, such impacts are of a much smaller magnitude than in the industries mentioned above. Examples of such potential changes in SO_x emissions, depending on the process implemented, are found in the chlor-alkali industry and others subsequently discussed in this report.

TABLE 20. ESTIMATED SO_x EMISSION FACTORS - PRIMARY COPPER INDUSTRY

Process	Emission factor* - no control (lb/ton of copper)			Emission factor* -with control (lb/ton of copper)			Control Efficiency
	Process	Power boiler	Total	Process	Power boiler	Total	%
Base case:							
Conventional smelting	4,620	23	4,643	1,400	5	1,405	70
• Outokumpu flash smelting	4,620	21	4,641	133	5	138	97
• Noranda	4,620	21	4,641	133	5	138	97
• Mitsubishi	4,620	21	4,641	133	5	138	97
• Arbiter	--	284	284	--	62	62	78

*Reported as lb SO_2/ton of anode copper.

TABLE 21. ESTIMATED CONTROLLED SO_x EMISSIONS - COPPER SMELTING

Process	Controlled SO_x emission factor (lb/ton of anode copper) Process	Power boiler	Total	Change in Emission factor	SO_x emissions (10^6 lb/yr) 1974	1989-1974*
Base case:						
Conventional smelting	1,400	5	1,405	--	2,250**	1,550
• Outokumpu flash smelting	133	5	138	-1,267	--	152
• Noranda process	133	5	138	-1,267	--	152
• Mitsubishi process	133	5	138	-1,267	--	152
• Arbiter	--	62	62	-1,343	--	68

*Based on increment in production from 1974 to 1989 of 1.1 million ton/yr. (Table 1)

**Estimated 1974 emissions, based on the emission factor of 1,405 lb SO_x/ton of anode copper, are $1,405 \times 1.6 \times 10^6 = 2,250 \times 10^6$ lb/yr.

Base Case Process - Graphite Anode Diaphragm Cell

The graphite anode diaphragm cell was selected as a basis for judging the energy and environmental effects resulting from the process changes studied, i.e., conversion to modified anodes and conversion to modified diaphragms, both changes being aimed at energy conservation.

Chlorine and caustic soda are produced by the electrolysis of brine. In the diaphragm cell, chlorine is formed at the graphite anode, while sodium ions migrate through the cell diaphragm to the cathode where a dilute solution of NaOH is produced. A more complete description of this process is presented in Volume XII, pages 21-25.

The electrolysis of brine is an energy-intensive process, requiring about 3,274 kWh/ton of chlorine. In addition, the plant requires 7,368 lb of low-pressure steam/ton of chlorine for caustic evaporation and brine heating. Sulfur dioxide emissions from power generation are estimated at 41.3 lb SO_x/ton of chlorine if the NSPS for coal-fired units is met. Without flue gas desulfurization, emissions are estimated at 190 lb/ton of chlorine. It was assumed (Volume XII, page 26) that the steam would be generated with byproduct hydrogen supplemented with natural gas. Hence, sulfur dioxide emissions from steam generation may be assumed to be nil.

Process Option 1 - Dimensionally Stable Anode (DSA)

The dimensionally stable anode (DSA) constructed of titanium and coated with precious metal/rare earth oxides offers numerous advantages over the graphite anode which result in power savings of up to 20%. The anode area and anode-cathode spacing of the DSA remains constant through out use, thereby preventing increased voltage requirements over time. Additional characteristics of the DSA are presented in Volume XII, pages 44-47. The DSA diaphragm cell process requires 3,151 kWh and 6,402 lb of steam/ton of chlorine. Steam is generated by the byproduct hydrogen and natural gas; hence, SO_x emissions are assumed to be nil.

Sulfur Dioxide emissions from power generation are estimated at 39.7 lb SO_x/ton of chlorine, if the NSPS for coal-fired units is met and 183 lb SO_x/ton of chlorine, if the emissions are uncontrolled, a slight improvement over the base case.

Process Option 2 - Expandable DSA

Cell power consumption can be reduced further by decreasing the gap between the anode and the cathode. With the rigid DSA, a "working" space must be allowed to assemble the cell. The expanded DSA is constructed so that the electrodes can be moved inward after the cell is assembled. This reduced spacing results in a reduction of about 325 kWh/ton of chlorine compared to the rigid DSA configuration. If emissions are controlled to meet the NSPS, then this power savings reduces

sulfur dioxide emissions to about 35.6 lb SO_x/ton of chlorine from the emissions estimated for the rigid DSA cells, a 14% reduction when compared with the conventional graphite anode process. If emissions are uncontrolled, then this power savings reduces emissions by 19 lb/ton of chlorine to 164 lb SO_x/ton of chlorine.

Process Option 3 - Polymer-Modified Asbestors

By replacing the conventional asbestos diaphragm by one which is polymer-treated and is baked into place on the cathode, power consumption can be reduced because diaphragm swelling does not occur. Electrical consumption may be reduced by as much as 280 kWh/ton if an extra wide anode is used. Thus, if flue gas is treated at the power source to meet the NSPS, then SO_x emissions are estimated to be 38.2 lb/ton of chlorine, or 3.1 lb/ton less than the emissions estimated for the rigid DSA cells with standard diaphragms. Thus, compared to the base case, the controlled SO_x emissions are reduced by 12%.

Process Option 4 - Polymer Membranes

Microporous Teflon-type polymer membranes which would replace the asbestos diaphragm entirely are being developed. These would give an energy performance equivalent to the polymer modified asbestor with the "extra wide" anode. Hence, the controlled and uncontrolled emissions would be identical to those of Process Option 3.

Process Option 5 - Ion Exchange Membranes

These membranes would separate the anode and cathode compartments of the cell and would allow the diffusion of sodium ions to the cathode but would not allow the diffusion of hydroxyl ions to the anode. Thus, the ion exchange cell is capable of producing a 25 to 40% caustic solution, whereas the standard cell produces a 10% caustic solution.

Energy use for a DSA with an ion exchange cell producing 40% NaOH is 2,980 kWh and 1,466 lb steam/ton of chlorine. Significantly less steam is required since a rather concentrated NaOH solution is produced directly from the cell.

Sulfur dioxide emissions from power generation are estimated to be 37.6 lb/ton of chlorine if the NSPS for coal-fired boilers is met. If flue gas is untreated, then emissions would be about 173 lb/ton of chlorine.

Process Option 6 - Mercury Cells

Chlorine and caustic can also be produced in a mercury cell. In a mercury cell, brine flows through a slightly sloped trough. At the dimensionally stable anodes, located at the top cover of the trough, chlorine is produced. A dilute sodium amalgam is produced at the cathode (a thin layer of mercury which flows along the bottom of the trough).

a 50% caustic solution is produced from the amalgam; and the mercury is recycled to the cell. Energy requirements for the mercury cell include 3,714 kWh of power and 550 lb of steam/ton of chlorine.

Sulfur dioxide emissions produced by power generation are estimated at 46.8 lb/ton of chlorine if the NSPS for coal-fired boilers is met. If flue gas is untreated, then emissions would be about 215 lb/ton of chlorine.

Summary

The emissions factor and total emissions for the base case and alternative processes are presented in Table 22. The mercury cell is estimated to result in a 13% yearly increase from the base case because of the relatively larger power requirements. The modified anodes and modified diaphragm options offer a 4 to 14% yearly reduction in SO_x emissions (up to 67 million lb/hr) from the base case process. On a national basis, these changes are small compared to those examined in the aluminum sector which also depends, to a large extent, on electric energy.

IRON AND STEEL

Recovery of Carbon Monoxide from BOP Vessels

Base Case Process - Complete Combustion System--

The base case process is a complete combustion system. The gases issuing from the mouth of the furnace are collected in a hood with considerable infiltration of air, burned in the hood, and cooled and cleaned of particulates before being released to the atmosphere. A detailed description of this system is presented in Volume III, page 18.

The combustion system consumes 14 kWh of electricity per ton of steel; this electricity is required for the operation of the heat scrubber system. Sulfur dioxide emissions from the power boiler are estimated at 0.8 lb/ton of steel, if the emissions are uncontrolled, and 0.2 lb/ton of steel, if the emissions are controlled to meet the NSPS.

Alternative Process - Non-Combustion BOP Off-Gas Recovery System—

In the alternative process, carbon monoxide is collected and recovered from the BOP off-gas. Two prominent systems, the OG process and the IRSID-CAFL process, are quite similar and are discussed in Volume III, pages 19-22.

The off-gas (OG) process consumes about 8 kWh of electricity per ton of steel. Energy consumptions are less than those for the combustion system as a result of the lower gas volumes handled in the non-combustion systems. Sulfur dioxide emissions from the power boiler are estimated at 0.5 lb/ton of steel, if the emissions are uncontrolled,

TABLE 22. ESTIMATED CONTROLLED SO_x EMISSIONS - CHLOR-ALKALI INDUSTRY

Process	Controlled SO_x emission factor (lb/ton of chlorine)			Change in emission factor	SO_x emission (10^6 lb/yr)	
	Process	Power boiler	Total		1974	1989-1974*
Base case: Graphite-anode diaphragm cell**	0	41.3	41.3	--	454**	491
• Dimensionally stable anodes	0	39.7	39.7	-1.6	--	472
• Expandable DSA	0	35.6	35.6	-5.7	--	424
• Polymer-modified asbestos	0	38.2	38.2	-3.1	--	455
• Polymer membrane	0	38.2	38.2	-3.1	--	455
• Ion exchange membrane	0	37.6	37.6	-3.7	--	447
• Modern mercury cell	0	46.8	46.8	+5.5	--	557

* Based on increment in production from 1974 to 1989 of 11.9 million ton/yr. (Table 1)

** Estimated 1974 emissions, based on the total emission factor of 41.3 lb SO_x/ton of chlorine, are $41.3 \times 11.0 \times 10^6 = 454 \times 10^6$ lb.

and 0.1 lb/ton of steel, if the emissions are controlled to meet the NSPS.

Blast Furnace

Base Case Process - Low Sulfur Blast Furnace Hot Metal--

The base case system is considered to include a blast furnace, cyclone, and venturi scrubber. The blast furnace sulfur content is completely controlled by adding limestone to form the sulfur-bearing slag and by limiting the sulfur content of the metallurgical coke. This process is further discussed in Volume III, page 29.

Most of the sulfur leaves the blast furnace in the liquid slag and hot metal; the off-gases contain only a negligible portion of the sulfur. Hence, sulfur dioxide emissions from the process are estimated to be nil.

Electricity consumed in the base case process is 0.25 kWh per ton of hot metal. Estimated emissions from the power boiler are 1.5 lb SO_x/ton of hot metal if the emissions are uncontrolled, and 0.3 lb SO_x/ton if the emissions are controlled to meet the NSPS.

Process Alternative - Blast Furnace with External Desulfurization--

Addition of an external desulfurization step is an alternative method of controlling the sulfur content of blast furnace hot metal. External desulfurization is achieved by injecting sulfur-reacting reagents (e.g., calcium or magnesium compounds carried in an inert gas such as nitrogen) into high-sulfur hot metal from a blast furnace. These compounds form a sulfide slag that is skimmed off prior to charging the hot metal to the BOP. Use of external desulfurization either permits limestone and coke ratios to be reduced, or allows the sulfur content in the coke to be increased without increasing the limestone charge to the furnace. A detailed description of this process is given in Volume III, page 31.

Sulfur dioxide emissions from the blast furnace off-gas are assumed to be nil. Electricity consumption in this alternative process is the same as the base case process, so power boiler emissions estimates are also the same. In neither case, is the contribution significant.

Quenching of Coke

Base Case Process - Wet Quenching--

In the base case process, the hot coke is pushed from the oven into a coke car where it is quenched with water. The steam which is produced is vented to the atmosphere. Excess water is allowed to drain and is often recirculated. Electricity consumed by the wet quenching process is not estimated in the analysis presented in Volume III, but it can be

assumed to be quite low.

Process Alternative Option - Dry Quenching--

In dry quenching of coke, the hot coke, pushed from the ovens, is cooled in a closed system. "Inert" gases extract heat from incandescent coke by direct contact. The heat is then recovered from the inert gases in a waste heat boiler or by other techniques.

The incremental electrical requirements are estimated at 8.4 kWh/ton of coke. Incremental emissions from the power boiler are estimated at 0.5 lb SO_x/ton of coke, if the emissions are uncontrolled, and 0.1 lb SO_x/ton of coke, if the emissions are controlled to meet the NSPS.

In addition, if the recovered heat, estimated at 1.1×10^6 Btu/ton of coke, is used in the plant, then an air emissions 'credit' may be realized. This credit is estimated to be 6.1 lb SO_x/ton of coke, if the emissions from the power boiler remain uncontrolled. The credit would be 1.2 lb SO_x/ton of coke, if the emissions were controlled to meet the NSPS.

Thus, the net incremental emissions credit is estimated to be 5.6 lb SO_x/ton of coke, if the emissions are uncontrolled, and 1.1 lb SO_x/ton of coke, if the emissions are controlled to meet the NSPS.

Steelmaking

Base Case Process - Coke Oven, Blast Furnace (BF), and Basic Oxygen Furnace (BOF) Route for Steelmaking--

The base case process is the conventional process for steelmaking. It is assumed, for our analysis, that 30% scrap metal is used in the BOP. A detailed description of the process is given in Volume III, page 54.

Electricity consumed by the coke oven, BF, BOF, and pollution control equipment is estimated at 120 kWh/ton of steel (Volume III, pages 79, 82-84). SO_x emissions from the power boiler are estimated at 7.0 lb/ton of steel, if the flue gas is untreated, and 1.5 lb/ton of steel if the NSPS is met.

Steam, consumed by the coke-making facilities, is required at about 670 lb/ton of steel. If this steam is generated with coal, then SO_x emissions are estimated at 3.7 lb SO_x/ton of steel if the flue gas emissions are uncontrolled, and 0.8 lb SO_x/ton of steel, if the flue gas is treated to meet the NSPS.

Process Option - Direct Reduction Route for Steelmaking--

Iron oxide pellets, ore lumps, and the like, can be partially reduced in the solid state by reaction with a reducing gas mixture. These

prereduced materials can partially or entirely replace purchased scrap in the steelmaking electric arc furnaces. In this alternative process, it was also assumed that 30% scrap is used with 70% prereduced pellets to make steel. A detailed process description is given in Volume III, page 54.

Electricity consumed by the sponge iron facilities, the electric furnace shop, and the pollution control equipment is estimated at 712 kWh/ton of steel. Sulfur dioxide emissions from the power boilers are estimated at 41.3 lb/ton of steel, if the emissions are uncontrolled, and 9.0 lb/ton of steel if the emissions are controlled to meet the NSPS.

Summary

The emissions factor and total emissions for the base case processes and the alternative processes are summarized in Table 23.

In the production of iron, it is seen that external desulfurization offers no reduction in SO_x emissions from the base case process, largely because most of the sulfur values leave the blast furnace area in the slag.

In the production of steel, recovery of the low-sulfur off-gas from the BOF offers a 50% reduction in emissions because of its waste heat value, which can potentially reduce need for high-sulfur fuels. However, steelmaking by the direct reduction method will result in nearly a three-fold increase in emissions over the conventional route because of the high power requirements of this alternative route.

PHOSPHORUS/PHOSPHORIC ACID

Base Case Process - Electric Furnace Production of Phosphorus and Conversion of Phosphorus to Phosphoric Acid

In this process, phosphate rock is reduced to elemental phosphorus by coke in an electric furnace. Phosphorus vapor and carbon monoxide are produced. The phosphorus is condensed and subsequently converted to pure phosphoric acid. The details of this process are presented in Volume XIII, pages 23-24.

Electric furnace production of phosphorus is a very energy-intensive operation. Electrical energy requirements are estimated at 13,000 kWh per ton of phosphorus (P_4). More than 90% of this energy is required by the furnace; the remainder is required for pumping operations. In addition, 1.9 tons of coke/ton of P_4 are charged to the furnace, where carbon monoxide is produced. The carbon monoxide is recovered and fired in the rotary kiln where the furnace feed materials are prepared. A small amount of natural gas (6 million Btu/ton of P_4) is required to supplement the carbon monoxide gas.

TABLE 23. ESTIMATED CONTROLLED SO_x EMISSIONS - IRON AND STEEL INDUSTRY

Process	SO_x emission factor (lb/ton of product) Process	Power boiler	Total	Change in emission factor	SO_x emissions (10^6 lb/yr) 1974	1989-1974*
Base case:						
BOP with no off-gas recovery	--	0.2	0.2	--	16.4**	12.0
• BOP with off-gas recovery	--	0.1	0.1	-0.1	--	6.0
Base case:						
Blast furnace	--	0.3	0.3	--	30**	13.4
• Blast furnace with external desulfurization	--	0.3	0.3	0.0	--	13.4
Base case:						
Wet quenching of coke	--	N.A.	N.A.	--	N.A.	N.A.
• Dry quenching of coke	-1.2***	0.1***	-1.1***	-1.1	--	-30.6***
Base case:						
Coke oven, blast furnace, BOP route	0.8	1.5	2.3	--	189**	138
• Direct reduction, EAF route	--	9.0	9.0	6.7	Small	540

(continued)

TABLE 23 (continued)

* Based on increment in production from 1974 to 1989 - 27.8×10^6 tons of coke, 44.8×10^6 tons of iron, and 60×10^6 tons of steel.

** Estimated 1974 emissions based on multiplying emission factor by 1974 production: 62 million tons coke, 100 million tons iron and 82 million tons BOP steel.

*** Emission factor is based on incremental requirements and credits of the dry-quench process as it compares to the wet-quench process.

N.A.: Not available - see footnote *** for dry quenching of coke.

Sulfur dioxide emissions result primarily from the coal-fired power boiler. It is estimated that 71.5 lb SO_x/ton of P_2O_5 are emitted if the NSPS for coal-fired units is met. Without flue gas desulfurization, emissions are estimated at 329 lb/ton of P_2O_5.

Sulfur dioxide emissions from the furnace coke are negligible since the sulfur in the coke would be removed with the slag by the calcium from the phosphate ore.

Process Option 1 - Chemical Cleanup of Wet-Process Phosphoric Acid

In the wet process, phosphate ore is reacted with sulfuric acid. Phosphoric acid (32% solution) is recovered from the undigested ore and the gypsum byproduct. This acid is concentrated by evaporation to the 54% P_2O_5 product. The wet process is described in more detail in Volume XIII, pages 35-37. However, there are a number of impurities in the regular wet-process phosphoric acid which make it unsuitable for use in certain applications. Wet acid is purified to sodium tripolyphosphate by a two-stage neutralization process (Volume XIII, page 49).

Steam is required to concentrate the acid solution. If the phosphoric acid plant is integrated with a sulfuric acid plant, then this steam is generated when the sulfur is oxidized, yielding 13 x 10^6 Btu/ton of P_2O_5 and controlled SO_2 emissions of 10 lb/ton of P_2O_5. Approximately half of the steam heat is used in the sulfuric acid plant and the other half is used by the phosphoric acid plant.

Electricity (250 kWh/ton of P_2O_5) is required to drive pumps, agitators, and filters in the wet-acid process. An additional 16 kWh/ton of P_2O_5 is required for the chemical cleanup of the acid. Sulfur dioxide emissions from power generation is estimated at 3.4 lb SO_x/ton P_2O_5, if the steam is generated from a coal-fired boiler which complied with the NSPS. Without sulfur dioxide control, emissions would be about 15.4 lb/ton of P_2O_5.

Process Option 2 - Solvent Extraction Cleanup of Wet-Process Phosphoric Acid

Cleanup of wet-process phosphoric acid is based on the fact that phosphoric acid can be transferred from solution in an aqueous phase to solution in an organic phase and leave behind undesirable impurities, such as calcium chloride, in the aqueous layer. The organic phase can then be contacted in a separate unit with fresh water to yield a pure solution of phosphoric acid. A detailed process description is given in Volume XIII, page 60.

The solvent-extraction process requires about 10,000 lb steam/ton of P_2O_5 for concentration of the acid from 15% as it is produced in the extraction section to a concentration of about 60% P_2O_5. If the steam is generated with low-sulfur oil so that flue gas desulfurization is not required, then emissions are estimated at 5.5 lb SO_x/ton of P_2O_5.

Electricity requirements will be about 300 kWh/ton of P_2O_5. The estimated SO_x emissions from power boilers are 3.8 lb/ton of P_2O_5, with no control, and about 17.4 lb/ton of P_2O_5 with control to meet the NSPS.

Summary

The emissions factor and total emissions for the base case process and alternative processes are summarized in Table 24. Both of the process options for "pure" phosphoric acid offer a significant reduction in SO_x emissions over the base case process. This reduction is primarily a result of the lower power requirements for both the chemical cleanup and solvent extraction process options.

FERTILIZERS

Nitric Acid Production

The manufacture of nitric acid, described in Volume XV, pages 25-28, generates significant emissions of nitrogen oxide and this area of primary interest is discussed in more detail in "Volume XV, NO_x Summary Report". Adoption of air pollution control is a recent practice in the industry. The process change considered in the nitric acid production is the application of alternative NO_x abatement systems. These processes are described in Volume XV, pages 33-42.

Base Case Process - Nitric Acid Production without NO_x Emission Control--

Nitric acid is produced by the oxidation of ammonia, usually under high pressure and temperature over a platinum catalyst. Waste heat recovered from the product gases is used to generate steam. The cooled gases are subsequently sent to an absorption tower to form the acid product.

Fuel requirements are satisfied by natural gas. Steam generated by the waste heat is included as an energy credit. An analogous credit for SO_x emissions was assumed, since the steam generated by the waste heat would otherwise be generated by low-sulfur oil so that flue gas desulfurization would not be required. This emissions credit is estimated to be 0.4 lb SO_x/ton of nitric acid.

Process Option 1 - Catalytic Reduction--

In the catalytic reduction process, tail gas from the absorber passes through a combustor where the nitrogen oxides are reduced to N_2 and O_2. Natural gas is used as a fuel in the combustor. Steam is generated by waste heat recovered from the product gases.

Energy requirements for the process include natural gas and electricity. Although catalytic reduction is an energy-intensive process, there is an SO_x emissions credit because steam, which would otherwise

TABLE 24. ESTIMATED CONTROLLED SO_x EMISSIONS - PHOSPHORUS/PHOSPHORIC ACID PRODUCTION

Process	SO_x emission factor ($lb/ton\ P_2O_5$) Process	Boiler	Total	Change in emission factor	SO_x emissions (10^6 lb/yr) 1974	1989-1974 *
Base case:						
Electric furnace**	0	71.5	71.5	--	100**	45.0
• Chemical cleanup of wet-process acid	10.0	3.4	13.4	-58.1	--	8.4
• Solvent extraction of wet-process acid	5.5	3.8	9.3	-62.2	--	5.9

* Based on the incremental production detergent grade phosphoric acid from 1974 to 1989 of 0.63×10^6 lb/yr multiplied by total emission factor.

** The SO_x emissions based on the emission factor of 71.5 lb/ton of detergent-grade phosphoric acid in the year 1974 are $71.5 \times 1.4 \times 10^6 = 100 \times 10^6$ pounds.

be generated by oil, is generated with waste heat from the process. The net SO_x emissions credit is estimated to be 0.6 lb SO_x/ton of nitric acid.

Process Option 2 - Molecular Sieve Method--

This method is based on the principles of adsorption, oxidation, and regeneration of the molecular sieve. An oil-fired heater is used to provide heat for regeneration of the sieve. The process has high efficiency for removal of NO_x gases. A detailed description of the method is given in Volume XV, page 36.

Energy requirements include fuel oil, steam, and electricity. High power requirements (26 kWh/ton of acid) result from the added compression requirements and the need to regenerate the sieve. SO_x emissions from power boilers without flue gas desulfurization are estimated to be 1.5 lb SO_x/ton of acid, and 0.3 lb SO_x/ton of acid from power boilers with flue gas desulfurization required to meet the NSPS. SO_x emissions from the fuel oil (0.5% sulfur) used in the sieve regeneration and steam production are estimated at 11.1 lb/ton of acid, for a total of 11.4 lb.

Process Option 3 - Grand Paroisse or Extended Water Absorption--

In this process, tail gas from the existing absorption tower is delivered to a second absorption tower for "extended absorption of nitrogen oxides by water".

The energy requirements for this process are small -- only 7.2 kWh/ton of nitric acid product are used. Power plant emissions are estimated at 0.1 lb SO_x/ton of acid, if the NSPS for coal-fired units is met, and 0.4 lb SO_x/ton of acid for plants without flue gas desulfurization.

CDL/Vitok Process--

In this process, the tail gas is scrubbed with nitric acid under conditions which reduce the nitrogen oxides to the desired level. Energy requirements include steam and electricity. The total steam requirements will result in SO_x emissions of 31.5 lb/ton of acid, if low-sulfur fuel oil is used, so that flue gas desulfurization is not required. Electrical requirements (24 kWh/ton of acid) will result in SO_x emissions of 0.3 lb/ton of acid, if the flue gas is desulfurized to meet NSPS for coal-fired, and 1.4 lb/ton, if no desulfurization is performed.

The Masar Process--

In this process, the tail gas is chilled and then scrubbed with an urea-containing solution. As nitric acid is produced, urea hydrolyzes and forms ammonium nitrate.

Steam is consumed at 105,000 lb/ton of acid, and electricity, at 1.5 kWh/ton of acid for this process. Steam generation by low-sulfur fuel oil will result in 57.6 lb SO_x/ton of acid. The electrical requirement contributes essentially no SO_x emissions, whether or not the power boilers meet the NSPS for coal-fired units.

Conversion to Fuel Oil in Mixed Fertilizer Plants Equipped with Bag Filters

Base Case Process--

The base case operation is an ammoniation granulation plant which uses a natural gas-fired dryer and is equipped with a baghouse filter to control fertilizer dust produced during drying. Only 20 percent of the estimated 200 plants is equipped with baghouses and would therefore be affected by this process change. Sulfur dioxide emissions from the base case operation are essentially nil.

Installation of Scrubber on Baghouse-Equipped Plants when Converting from Natural Gas to Fuel Oil--

When fertilizer dryers were converted from natural gas to oil, operational problems sometimes resulted from the plugging of the baghouse filters with ash from the oil. If these problems cannot be resolved by the modification of the combustion process, then wet scrubbers will be required for particulate control.

Incremental SO_x emissions result from conversion to fuel oil assumed to contain 0.5% sulfur. If 20% of the sulfur dioxide is removed in the wet scrubber, then SO_x emissions are estimated to be 0.14 lb/ton of fertilizer; no further specific control for SO_x is anticipated.

Continued Operation of the Baghouse Filter after Conversion from Natural Gas to Fuel Oil--

If filter clogging problems can be alleviated by proper design and operation of the fuel oil-fired dryer, the baghouses will not have to be replaced by scrubbers. If the fuel oil contains 0.5% sulfur, and since 0.3 million Btu of fuel are required to dry each ton of fertilizer (Volume IV, page 54), then 0.18 lb SO_x will be emitted per ton of product by conversion to fuel oil.

Summary

The emission factors and total emission for the base case and alternative processes for NO_x abatement and fuel conversion in fertilizer drying are presented in Table 25. For NO_x abatement in nitric acid production, only the catalytic reduction process option offers a reduction of SO_x emissions from the base case process. This is primarily a result of the large power requirements for the NO_x control systems. On the contrary, the molecular sieve, CDL/Vitok, and Masar processes for NO_x

TABLE 25. ESTIMATED CONTROLLED SO_x EMISSIONS - FERTILIZER INDUSTRY

Process	SO_x emission factor (lb/ton of nitric acid) Process	Power boiler	Total	Change in emission factor	SO_x emissions (10^6 lb/yr) 1974	1989-1974*
Nitric acid production - With various processes to control NO_x emissions						
Base case: No NO_x control	-.4	0.0	-.4	--	-3.3**	-2.6
• Catalytic reduction	-.7	.1	-.6	-0.2	--	-4.0
• Molecular sieve	11.1	.3	11.4	11.8	--	75.2
• Grand Paroisse	0.0	0.1	0.1	0.5	--	0.66
• CDL/Vitok	31.5	0.3	31.8	32.2	--	209.0
• Masar	57.6	0.0	57.6	58.0	--	383.0
Converting fertilizer dryers (with baghouses) from natural gas to oil						
Base case: Natural gas	Nil	Nil	Nil	--	Nil	Nil
• Better equipment/ technique with fuel oil	0.18	0.0	0.18	0.18	--	0.29***
• Installing scrubbers	0.14	0.0	0.14	0.14	--	0.22***

(continued)

TABLE 25 (continued)

* Calculated using 4% growth rate for 15 years based on 10 million tons/year in 1974 and rising to 18 million tons/year in 1989; thus potential growth of 18×10^6 tons.

** Estimated 1974 emissions based on total emission factor (credit) of -0.4 lb SO_x/ton of nitric acid are $0.4 \times 8.2 \times 10^6 = -3.3 \times 10^6$ ton/yr (SO_x emissions credit since energy is recovered in this process).

*** Based on 4% growth rate for 15 years based on 2 million tons/yr in 1974 and rising to 3.6 million tons in 1989; this potential growth of 1.6 million tons is multiplied by the emission factor.

control may significantly increase estimated SO_x emissions.

Fuel conversion for fertilizer dryers equipped with baghouse filters has a small impact on the total amount of sulfur dioxide emissions on an industry-wide basis since only 20% of the fertilizer plants are equipped with these air filters.

TEXTILES

Two textile mills, an integrated knitting mill and an integrated weaving mill, were examined. The mill operation includes the knitting of the greige yarn, or the weaving of greige fabric, and the subsequent dyeing and finishing of the fabric.

Knit Fabrics Production

Base Case Process--

In the knitting mills, yarn is knitted into fabric in the greige mill. The greige fabric is next scoured to remove knitting oil, and is then dyed, washed, and spin-dried to remove as much water as possible before hot-air drying. A finish (softener/lubricant) is then applied to the fabric, which is dried and heat-set. Details of the knitting mill operation are presented in Volume IX, page 33.

It is unlikely that natural gas, used for the hot-air drying and heat-set operations, will be easily replaced, as it is required by all of the equipment presently available for fabric drying and heat-setting operations.

Steam is used for the heat input to the scouring, dyeing, and washing operations. In the base case process, it was assumed that the steam would be generated with low-sulfur oil, so that flue gas desulfurization would not be required. Since 4 lb of steam/lb of fabric are required, then about 4.4 lb SO_x/ton of fabric would be emitted. Because of the relatively small energy requirements of textile mills, it seems unlikely that coal will be used as a fuel for steam production (Volume IX, page 41).

Electricity is required to provide mechanical energy to transfer fabric from the beginning to the end of the process line and for knitting the yarn into the fabric. Electrical requirements of 0.18 kWh/lb of fabric will result in SO_x emissions of about 4.5 lb SO_x/ton of fabric, if the NSPS is met. Without SO_2 cleaning of the stack gas, SO_x emissions would be 20.7 lb/ton of fabric.

Advanced Aqueous Processing--

The sequence of operation is similar to the base case except that (1) the hot air drier is replaced by an air/vacuum extractor, thereby reducing natural gas requirements and increasing electrical requirements,

and (2) the scouring, dyeing, and washing operations are modernized with more efficient equipment, thereby reducing steam requirements. The advanced process is described in detail in Volume IX, pages 35-37.

Steam requirements of 1.9 lb/lb of fabric will result in 2.1 lb SO_x/ton of fabric, if the steam is generated by low-sulfur oil so that flue gas desulfurization is not required. Electrical requirements of 0.25 kWh/lb of fabric will result in 6.3 lb SO_x/ton of fabric, if the NSPS are met. Without flue gas desulfurization, SO_x emissions would be 29 lb SO_x/ton of fabric.

Solvent Case—

Solvent systems are assumed for the scouring, dyeing, and finishing operations. The fabric is steam-stripped to remove residual solvent. Clean solvent is recovered by distillation with steam. Details of a solvent process are provided in Volume IX, pages 37-41.

Steam requirements of 1.1 lb/lb of fabric will result in 1.2 lb SO_x/ton of fabric, if low-sulfur oil is used to generate the steam and flue gas desulfurization is not required.

Electricity requirements of 0.12 kWh/lb of fabric will result in 3.0 lb SO_x/ton of fabric, if the NSPS are met. Without SO_2 removal from the boiler flue gas, emissions would be about 13.8 lb SO_x/ton of fabric. By comparison with current technology, the solvent processing route can reduce SO_x emissions -- after control -- by some 53%.

Woven Fabrics Production

Base Case Process--

The operations of woven fabric preparation, dyeing, and finishing, involve a much longer processing sequence than knit fabrics. These steps are described in Volume IX, page 44.

Natural gas is used in the drying, setting, and curing operations; hence there are no SO_x emissions in these steps. Steam (15 lb/lb of fabric) is used for process water heating in the dyeing, washing, and finishing steps. Steam generation will result in 16.5 lb SO_x/ton of fabric, if low-sulfur oil is burned and flue gas desulfurization is not required. Electrical energy requirements are estimated at 0.29 kWh/lb of product. This will result in SO_x emissions of 7.3 lb/ton of fabric, if the NSPS are met. Otherwise, uncontrolled emissions are estimated at 33.6 lb/ton of fabric.

Advanced Process--

The advanced processing includes a polyvinyl alcohol (PVA) recovery loop which recycles concentrated PVA solution back to sizing and the hot water back to the desizing operation. Details of the advanced

case sequence are presented in Volume IX, page 49.

Steam requirements have been reduced to 6.4 lb/lb of fabric by reduction in overall process water use and recycling of wash waters. This steam generation will produce 7.0 lb SO_x/ton of fabric. These emissions are not controlled. Electrical requirements have been reduced to 0.15 kWh/lb of steam, which will result in SO_x emissions of 3.8 lb/ton of fabric, if the NSPS are met. Without control, sulfur dioxide emissions are estimated at 17.5 lb/ton of fabric.

Summary

The emissions factor and total emissions for the base case process and alternative processes are summarized in Table 26. The SO_x emissions from the advanced aqueous process for the knitted fabric are slightly lower than those from the base case process; both are relatively small compared to other SO_x emissions in the industrial sector. However, SO_x emissions from advanced aqueous processing of woven fabrics are about 50% lower than those from the corresponding base case processes.

TABLE 26. ESTIMATED SO_x EMISSIONS - TEXTILE INDUSTRY

Process	SO_x emission factor (lb/ton fabric) Process	Power boiler	Total	Change in emission factor	SO_x emissions (10^6 lb/yr) 1974	1989-1974*
Knit fabric						
Base case - aqueous	4.4	4.5	8.9	--	2.9**	1.1
• Advanced aqueous	2.1	6.3	8.4	-.5	--	1.0
• Solvent processing	1.2	3.0	4.2	-4.7	--	0.5
Woven fabric						
Base case - aqueous	16.5	7.3	23.8	--	50***	19.3
• Advanced aqueous	7.0	3.8	10.8	-13.0	--	8.8

* Based on no retirement of existing facilities, incremental production from 1974 to 1989 of 1) 0.12×10^6 ton/yr (knit fabric) multiplied by total emission factor, and 2) 0.81×10^6 ton/yr (woven fabric) multiplied by total emission factor.

** Estimated 1974 emissions from knit fabric production based on the total emission factor of 8.9 lb SO_x/ton of fabric are $8.9 \times 0.32 \times 10^6 = 2.85 \times 10^6$ lb.

*** Estimated 1974 emissions from woven fabric production based on total emission factor of 23.8 lb SO_x/ton of fabric are $23.8 \times 2.1 \times 10^6 = 50 \times 10^6$ lb/yr.

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